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Study Leading to the Development of Polymers for Use

in High Temperature

by

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Final Summary Report

October 1, 1962

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I. Abstract

A comparative study of three approaches to the synthesis of sulfamide has shown that reaction of sulfuryl chloride with excess liquid ammonia at low temperatures can be used to prepare the compound with reasonable efficiency.

A program for the preparation of polymeric, high temperature stable substances, based upon compounds belonging to the ammonio-sulfuric acid system, has been instituted. For this purpose, a series of ammonolysis and aminolysis reactions of sulfamide and of *N,N*-dialkylsulfamyl chlorides with a variety of aliphatic and aromatic amines have been carried out, and several new *N*-substituted derivatives of sulfamide have been prepared and characterized. Their liquid ranges and thermal stabilities have been evaluated also.

The reaction of sulfuryl chloride with primary and secondary diamines by the two-liquid phase procedure has failed to produce polymeric inorganic-organic materials. On the other hand, when sulfamide is allowed to react with aliphatic polyamines without solvent, deammonation takes place readily with the formation of definite products. Monomeric compounds are attainable by melt-polymerization at 90°C., whereas a linear polymer is produced when 1,6-hexane-diamine reacts with sulfamide under appropriate conditions.

The reaction of sodium hydrosulfide with sulfur in liquid ammonia has been found to be a convenient method for the synthesis of anhydrous sodium polysulfides. Non-metal polysulfides have been obtained by treating the hydrosulfide-sulfur solution in ammonia with a diacid chloride such as methylene chloride.

Sulfamic acid, sulfamide, and *N,N*-dialkylsulfamides have been found to react with phosphorus (V) chloride to give in good yields trichlorophosphazosulfonyl chloride, bis-trichlorophosphazosulfone, and the dialkylamides of trichlorophosphazosulfuric acid, respectively. Reactions of bis-trichlorophosphazosulfone and of the dialkylamides, of trichlorophosphazosulfuric acid with Grignard reagents have lead to compounds in which the chlorine atoms are all replaced by aryl groups.

The synthesis of sulfamuric chloride by thermal cleavage of trichlorophosphazosulfonyl chloride has been successfully effected. Inasmuch as two geometrical isomers are produced during the course of such thermal decomposition, the measurement of dipole moments has been used as a possible criterion for the assignment of their configurations.

Published papers based upon work completed under this contract include

- A. Vandi, T. Moeller, and L. F. Audrieth: "Synthesis and Properties of Some *N*-Substituted Sulfamides", *J. Org. Chem.*, **26**, 1136 (1961).
- A. Vandi, T. Moeller, and L. F. Audrieth: "Some Aminolysis and Deammonation Reactions of Dialkylsulfamyl Chlorides and Sulfamide with Polyamines", *J. Org. Chem.*, **26**, 3478 (1961).

A. Vandi and T. Moeller: "Nucleophilic Aromatic Substitutions Involving Bis-Trichlorophosphazosulfone and the Dialkylamides of Trichlorophosphazosulfuric Acid", Chem. and Ind., 1962, 221.

T. Moeller and A. Vandi: "Reactions of Bis-Trichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric Acid with Certain Grignard Reagents", J. Org. Chem. (In press)

In addition, a manuscript dealing with the sulfanuric chlorides and several manuscripts covering the syntheses of various compounds are in preparation.

II. Synthesis of Sulfamide

A. Introduction

The preparation of sulfamide has usually been attempted via the ammonolysis of sulfuryl chloride, either with ammonia or with an ammonium salt, amide, or imide that might be expected to yield ammonia in controlled quantity. A review of described procedures (1) indicates that none of these is notably efficient and that many yield only negative results. Of the procedures employing ammonia, those described by Kirsanov (2) and by Goehring et al., (3) appear most promising. These have been rechecked in the preliminary phases of this study, largely to provide sulfamide for use in other areas of investigation. A single variant of the reaction involving an ammonium salt has been examined.

B. Experimental

1. Ammonolysis of Sulfuryl Chloride by Ammonia According to the Procedure of Kirsanov (2) as Modified by Snyder (1). -- The procedure used was as follows: A 3-liter, wide-mouthed jar, equipped with a mechanical stirrer, a thermometer, and a gas inlet tube, was placed in an ice-salt bath contained in a large battery jar. Seven hundred fifty milliliters of carbon tetrachloride was added to the reaction jar and the whole cooled to -8°C . A strong current of ammonia was bubbled through the cooled carbon tetrachloride while a solution of 125 ml. of sulfuryl chloride in 625 ml. of carbon tetrachloride was added in 10-15 ml. increments. After each addition, the mixture was cooled to -8°C . before more of the halide was introduced. After all of the sulfuryl chloride had been added, the current of ammonia was maintained for an additional 30 minutes.

The white, pasty product was treated with water and the carbon tetrachloride removed by using a separatory funnel and then boiling. Ammonium chloride was largely removed by a series of vacuum evaporations on the steam bath and subsequent filtrations. The resulting thick, viscous mass was hydrolyzed by boiling with 0.5 N hydrochloric acid. After removal of more water by vacuum evaporation, the product was extracted several times, using a Soxhlett apparatus, with acetone and ethylacetate. The solvent was removed by evaporation and the resulting yellow crystals dissolved in boiling 95% ethanol. Cooling then gave white crystals of sulfamide. Yield: 11.7 g. (7.9%); 8.3 g. (5.6%), based on the sulfuryl chloride used.

2. Ammonolysis of Sulfuryl Chloride by Ammonia According to the Procedure of Goehring (3) as Modified by Eibeck (4). -- The most effective procedure was as follows: A 2-liter, 3-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a vent attached to a drying tube, was cooled to ca. -70°C . by means of a Dry Ice-chloroform bath. Some 300 ml. of liquid ammonia was then condensed into the flask at -70°C . A solution consisting of 50 ml. of sulfuryl chloride in 400 ml. of petroleum ether (b.p. $90-110^{\circ}\text{C}$.) was then added dropwise and with vigorous stirring over a period of 160 minutes, with the temperature remaining within $3-4^{\circ}$ of -70°C . The flask was then allowed to warm over night to room temperature to remove unreacted ammonia. The ether layer was removed and the product dried at room temperature. Two extractions, each with 250 ml. of ethyl acetate, were carried out. From each, white crystals resulted upon evaporation of the solvent. The remaining solid was dissolved in a solution obtained by diluting 15 ml. of 12 *N* hydrochloric acid to 100 ml. with water. This solution was evaporated and the brown solid obtained extracted with ethyl acetate. The combined crystals from the three ethyl acetate extractions were dissolved in boiling 95% ethanol. Cooling gave white, crystalline sulfamide. Yield: 27.86 g. (46.5%). Comparable runs where acetone was used for the initial extraction gave yields of only 8.7 g. (14.6%); and 11.0 g. (18.8%).

3. Attempted Ammonolysis of Sulfuryl Chloride with Ammonium Chloride in Symmetrical Tetrachloroethane. -- The procedure employed was as follows: a mixture of 13.5 g. (0.1 mole) of sulfuryl chloride and 10.7 g. (0.1 mole) of ammonium chloride was refluxed in 500 ml. of tetrachloroethane for 9 hours, escaping vapors being trapped in 2 *M* sodium hydroxide solution. The solution in the trap was then neutralized with nitric acid and its chloride content determined by Mohr titration. Approximately 0.2 mole of chloride ion was found, suggesting that ammonolysis had occurred with release of hydrogen chloride. However, 0.1 mole of ammonium chloride was recovered from the initial reaction mixture. Since the liquid had changed from colorless to yellowish, it was reasonable to assume that the solvent had undergone reaction. Repetition of the experiment with omission of the ammonium chloride, gave 0.2 mole of chloride ion in the trap, indicating only reaction of sulfuryl chloride with tetrachloroethane and no ammonolysis.

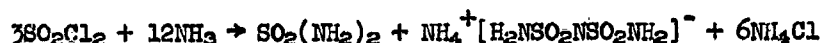
C. Discussion

Much of the tediousness and inefficiency of the Kirsanov procedure is eliminated by an adaptation of the Goehring method. The reported yield of 42% (av.) can be duplicated, if suitable precautions are taken. In every instance where lower yields resulted, acetone was used as a primary extraction solvent. This resulted in the formation of large quantities of reddish-black, tarry material, which apparently interfered with ultimate conversion to sulfamide. This difficulty is eliminated by use of ethyl acetate and by never evaporating above room temperature.

If a stated yield of ca. 40% is assumed to be a reasonable average for the Goehring procedure, the overall conversion in terms of the equation



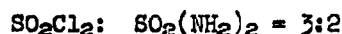
does not suggest this to be a particularly practical process. However, there is every evidence (3) that the initial process yields imidodisulfamide as well



Subsequent hydrolysis of the latter



indicates a total conversion to sulfamide in the mole ratio



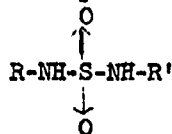
Thus a yield of 27.86 g. (p. 3), which amounted to 46.5% on the basis of 1:1 correspondence between sulfuryl chloride and sulfamide, becomes 70.5% on the basis of the second path. Evaluation in terms of the ammonium chloride recovered is in good agreement with this figure.

Formation of imidodisulfamide by direct reaction of sulfuryl chloride with ammonia plus lack of reaction of sulfuryl chloride with ammonia chloride, a poorer source of ammonia, suggest that direct formation of sulfamides must require more basic conditions than have been achieved here. In a measure, these are compensated for by the presence of a large excess of ammonia at all times, but even then some deammonation must occur. It is conceivable that the presence of basic ions in the ammonia would limit imidodisulfamide formation and thereby improve the yield.

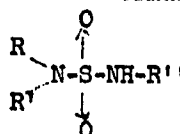
III. N-Substituted Derivatives of Sulfamide

A. Introduction

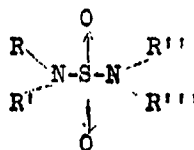
Material included in this report relates to synthesis and characterization only. The synthesis program involved the preparation of a number of N,N'-disubstituted, N,N,N'-trisubstituted, and N,N,N',N'-tetrasubstituted sulfamides, which may be represented by the following generalized formulas:



I



II



III

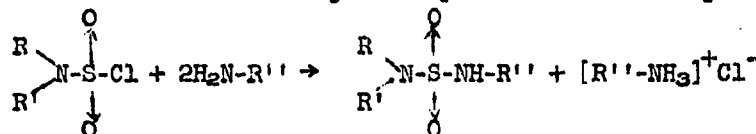
Thus far, only compounds relating to formulas II and III have been prepared, where:

$R = R' = \text{an alkyl radical}$

R'' and R''' may be alkyl, aryl, alkaryl, or heterocyclic radicals.

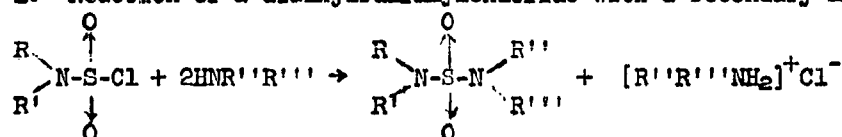
A survey of the literature revealed the following general synthetic methods for the preparation of N,N,N' -trisubstituted and N,N,N',N' -tetrasubstituted sulfamides.

1. Reaction of a dialkylsulfamyl chloride with a primary amine.



This reaction is the most frequently reported method for the preparation of symmetrical and unsymmetrical trisubstituted sulfamides. Chloroform (5), benzene or ether (6) have been used as solvents for carrying out the reaction. An excess of primary amine, to react with the hydrogen chloride released, is usually used as acid acceptor.

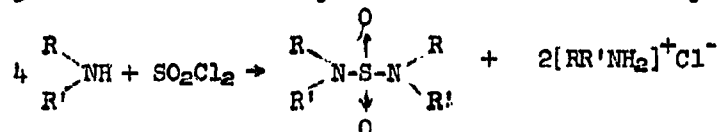
2. Reaction of a dialkylsulfamylchloride with a secondary amine.



This reaction is the most frequently reported method for the preparation of symmetrical and unsymmetrical tetrasubstituted sulfamides.

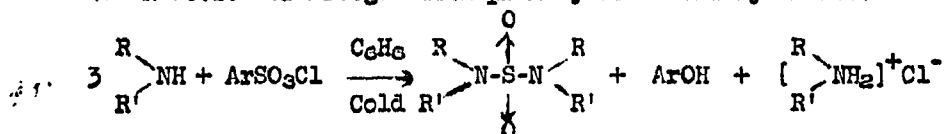
Chloroform (5) has been used as a solvent for carrying out the reaction, and an excess of secondary amine has been used to react with the hydrogen chloride which is evolved.

3. Reaction of sulfuryl chloride with a secondary amine.



This method, which yields symmetrical tetrasubstituted sulfamides and is carried out in cold benzene, is reported in the literature in a patent (7).

4. Reaction of ArSO_3Cl with primary or secondary amines.



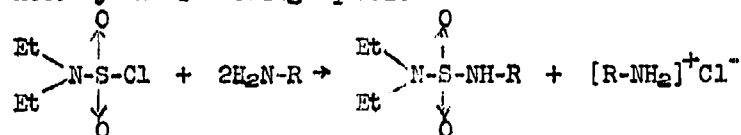
This method also yields symmetrical tetrasubstituted sulfamides. (8)

During this investigation, 9 trisubstituted and tetrasubstituted sulfamides were prepared and characterized. Of the compounds synthesized, 7 are new compositions of matter not reported in the literature.

All these compounds were prepared by allowing diethylsulfamylchloride (1/mole) to react with a primary or secondary amine (2 moles) and refluxing in chloroform or ether as solvent.

For this purpose diethylsulfamylchloride has been prepared either by refluxing diethylamine hydrochloride with an excess of redistilled sulfuryl chloride (5) or by adding pure diethylamine dropwise to an excess of redistilled sulfuryl chloride (9). The latter procedure gives better results than the first one and also, according to the literature, the yield is more satisfactory. Diethylsulfamyl chloride is a colorless liquid which boils at 75°C. at 3 mm.

The reaction of diethylsulfamylchloride with a primary amine is represented by the following equation:



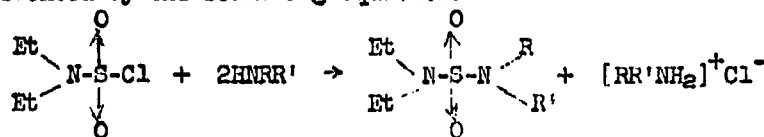
Where: R = H, C₄H₉-, C₆H₅-, C₆H₁₁-

The following trisubstituted sulfamides were prepared by this type of reaction.

- I. N, N-diethylsulfamide
- II N,N-diethyl-N'-butylsulfamide
- III N,N-diethyl-N'-cyclohexylsulfamide
- IV N,N-diethyl-N'-phenylsulfamide

All of these compounds except N,N-diethylsulfamide were prepared in this way. N,N-diethylsulfamide was prepared by adding the pure diethylsulfamylchloride dropwise to an excess of liquid ammonia (5) with vigorous agitation over a period of 2 hours, followed by evaporation of the excess of liquid ammonia at room temperature. The pure product was obtained by means of several recrystallizations from ether.

The reaction of diethylsulfamylchloride with a secondary amine is represented by the following equation:



Where: R = R' = C₄H₉-

[R = C₆H₅

R' = CH₃

[R = C₆H₁₁-

R' = CH₃

R = R' is a heterocyclic group such as morpholine or

The following tetrasubstituted sulfamides were prepared by this type of reactions.

- V N,N-diethyl-N',N'-dibutylsulfamide
- VI N,N-diethyl-4-morpholinesulfamide
- VII N,N-diethyl-4-piperidinesulfamide
- VIII N,N-diethyl-N'-phenyl-N'-methylsulfamide
- IX N,N-diethyl-N'-cyclohexyl-N'-methylsulfamide

B. Physical Properties

Tri- and tetrasubstituted sulfamides are generally colorless oily materials. When they are solids, they have very low melting points and are very difficult to recrystallize. Normal heptane was found to be the best solvent for such recrystallizations. The compounds are soluble in all the common organic solvents but are insoluble in cold water. The trisubstituted sulfamides are soluble in alkali, owing to the presence of an acidic hydrogen atom, whereas the tetrasubstituted derivatives are insoluble.

C. Unsuccessful Preparations

Diethylsulfamylchloride does not react with diphenylamine, either in the presence of chloroform and benzene as solvents or in the absence of solvent. The mixture in the molar ratio 1:2 was refluxed for 48 hours, but after this period of time unreacted diphenylamine and diethylsulfamylchloride were obtained by distillation under vacuum.

Recently, it has been found that sulfamide when treated with amines yields mono- and disubstituted sulfamides. We tried to prepare the diphenylsulfamide by heating sulfamide and diphenylamine in the molar ratio 1:1 at 90-120°C. without solvent, with the intent of allowing the diphenylsulfamide to react subsequently with diethylamine.

Unfortunately no reaction occurs when sulfamide and diphenylamine are mixed together at 90-120°C. for three hours. Even after 3 hours heating at 160°C. only unreacted diphenylamine and a polymeric material, due perhaps to the polymerization of sulfamide, were obtained. An indirect way to prepare N,N-diethyl-N',N'-diphenylsulfamide was attempted too. Here, we tried to prepare the diphenylsulfamylchloride intending to react the latter with diethylamine. The mixture was then slowly poured into a flask fitted with a reflux condenser. The mixture was heated gently and held for 12 hours. After the removal of the excess of sulfurylchloride, the solid material was dissolved in hot benzene and recrystallized. The white product, after recrystallization from n-heptane, melts at 138-139°C. A test to check the presence of sulphur in the compound gave negative results. Microanalysis showed the substance to be $C_{24}H_{24}Cl_6N_4$, hexachlorodiphenylamine. According to the literature, that compound melts at 138-139° (10).

D. Experimental

The general conditions for the preparation of tri- and tetrasubstituted sulfamides are summarized in Table I and Table II, respectively. Analytical

data are given in Table III and physical constant data in Table IV.

Table I
Preparation of Trisubstituted Sulfamides

| | <u>Moles</u> | | <u>Reaction Conditions</u> | | <u>Temp.</u> (°C.) | <u>Time</u> (Hr.) |
|-----|---|--------------|--------------------------------|-------------------|-----------------------|----------------------|
| | <u>Et₂-N-SO₂-Cl</u> | <u>Amine</u> | <u>Acid</u> <u>Acceptor</u> | <u>Solvent</u> | | |
| II | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 8 |
| III | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 1 |
| IV | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 12 |

Table II
Preparation of Tetrasubstituted Sulfamides

| | <u>Moles</u> | | <u>Reaction Conditions</u> | | <u>Temp.</u> (°C.) | <u>Time</u> (Hr.) |
|------|---|--------------|--------------------------------|-------------------|-----------------------|----------------------|
| | <u>Et₂-N-SO₂-Cl</u> | <u>Amine</u> | <u>Acid</u> <u>Acceptor</u> | <u>Solvent</u> | | |
| V | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 1 |
| VI | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 2 |
| VII | 0.1 | 0.2 | Amine | CHCl ₃ | 0°C. | 12 |
| VIII | 0.1 | 0.2 | Amine | --- | 70°C. | 15 min. |
| IX | 0.1 | 0.2 | Amine | CHCl ₃ | 70°C. | 1 |

1. Diethylsulfamylchloride.-- Sulfurylchloride (134 g., 1.0 mole) was placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. The flask was surrounded with an ice bath, and diethylamine (73.5 g., 1.0 mole) was added dropwise to the sulfurylchloride with vigorous agitation. The reaction mixture was warmed and carefully poured into a flask, fitted with a reflux condenser. Gentle refluxing was continued for 24 hours. The viscous yellow material was cooled and washed with a dilute solution of Na₂CO₃. The oily material which was separated was dissolved in ether and dried over CaCl₂. The ether was distilled off leaving an oil.

The final product, obtained by means of vacuum distillation, was a colorless oil, b.p. 62°C./0.02 mm. Yield: 56.0 g. (35.0% based on the amine).

2. N,N-diethylsulfamide.-- Liquid ammonia (100 ml.) was placed in a three-necked flask fitted with a mechanical stirrer, an outlet tube and a small separatory funnel. The flask was surrounded with a bath of methylcellosolve and "dry-ice" to keep the temperature at -70°C . Diethylsulfamylchloride (20 g., 0.117 mole) was added dropwise in two hours with vigorous agitation. The solution was stirred for two hours, and the flask was kept at room temperature in order to allow the evaporation of the excess of liquid ammonia. The solid material was dissolved in hot ether. The suspension was filtered and the ether distilled off under vacuum.

The white crystalline compound, after two recrystallizations from ether, melts at 44°C . Yield: 9.5 g. (53.0%).

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_2\text{S}$: C, 31.57; H, 7.95; N, 18.41.

Found : C, 31.49; H, 7.72; N, 18.49.

3. N,N-diethyl-N'-butylsulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), butylamine (15.0 g., 0.2 moles), and 80 ml. of chloroform were placed in a flask fitted with a reflux condenser. The reaction mixture was held at 70°C . for 8 hours. The excess of chloroform was then distilled off, and the remaining dark oily material was shaken in a separatory funnel with ether (100 ml.) and water (200 ml.). The ether layer was dried over anhydrous CaCl_2 and the ether distilled off leaving a dark oily residue.

The product, obtained after two vacuum distillations, was a colorless oil, b.p. $87^{\circ}\text{C}/0.1\text{ mm.}$, n_D^{25} 1.4510.

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 46.16; H, 9.68; N, 13.45.

Found: C, 45.90; H, 9.48; N, 13.14.

4. N,N-diethyl-N'-cyclohexylsulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), cyclohexylamine (20 g., 0.2 moles), and 50 ml. of chloroform were placed in a flask equipped with a reflux condenser. Gentle refluxing was held at 70°C . for 1 hours. The excess of chloroform was then distilled off, and the dark residue was partitioned between water and ether and shaken in a separatory funnel. The ether layer was dried over CaCl_2 and the ether distilled off leaving a dark oily materials.

The product, obtained after vacuum distillation, was a colorless, viscous oil, b.p. $136^{\circ}\text{C}/1\text{ mm.}$ On standing the product solidified to a crystalline mass, which after recrystallization from n-heptane melts at 49°C . Yield: 14.0 g. (60%).

Anal. Calcd. for $\text{C}_{10}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$: C, 51.28; H, 9.47; N, 11.95.

Found : C, 50.80; H, 9.40; N, 11.85.

5. N,N-diethyl-N'-phenylsulfamide.--Diethylsulfamylchloride (17.1 g., 0.1 mole), aniline (18.6 g., 0.2 moles), and 100 ml. of chloroform were placed in a flask fitted with a reflux condenser. Gentle refluxing was held at 70°C. for 12 hours. The excess of chloroform was then distilled off, and the viscous residue was dissolved in ether and filtered. The ether was distilled off leaving a dark, viscous oily material.

The product, obtained after two vacuum distillations was a yellow-orange oil, b.p. 171°C./2.5 mm., n_D^{25} 1.5260.

Anal. Calcd. for $C_{10}H_{12}N_2O_2S$: C, 52.64; H, 7.06; N, 12.28.

Found: C, 52.48; H, 7.11; N, 11.95.

6. N,N-diethyl-N',N'-dibutylsulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), di-butylamine (25.8 g., 0.2 moles), and 100 ml. of chloroform were placed in a flask fitted with a reflux condenser. The reaction, slightly exothermic, was complete after 1 hour with gentle heating at 70°C. After the removal of the excess of chloroform, the dark residue was partitioned between ether and water by shaking in a separatory funnel. The ether layer was dried over anhydrous $CaCl_2$ and the ether distilled off, leaving a viscous, yellow oil.

The product, obtained after two vacuum distillations, was a colorless oil, b.p. 88°C./0.15 mm. n_D^{25} 1.4500.

Anal. Calcd. for $C_{12}H_{22}N_2O_2S$: C, 54.53; H, 10.68; N, 10.60.

Found : C, 54.35; H, 10.34; N, 10.31.

7. N,N-diethyl-4-morpholinesulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), morpholine (17 g., 0.2 moles) and 50 ml. of chloroform were placed in a flask equipped with a reflux condenser. The reaction, initially very vigorous, required external cooling; then gentle refluxing was held at 70°C. for 2 hours. After the removal of the hydrochloride by means of filtration, the excess of chloroform was distilled off. The residue was then partitioned between ether and water by shaking in a separatory funnel. The ether layer was dried over $CaCl_2$ and the ether distilled off, leaving a viscous oily material.

The product, obtained from vacuum distillation, was a colorless oil, b.p. 91°C./0.15 mm., n_D^{25} 1.4695. Yield: 14 g. (70%).

Anal. Calcd. for $C_8H_{12}N_2O_3S$: C, 43.24; H, 8.16; N, 12.61.

Found : C, 43.13; H, 8.25; N, 12.44.

8. N,N-diethyl-4-piperidinesulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), piperidine (17 g., 0.2 moles), and 100 ml. of chloroform were placed in a flask fitted with a reflux condenser. The very exothermic reaction required external cooling, and then the mixture was held overnight at room temperature. After the removal of the hydrochloride by means of filtration, the excess of chloroform was distilled off. The residue was partitioned between ether and water by shaking in a separatory funnel. The ether layer was dried over anhydrous $CaCl_2$ and the ether distilled off, leaving a viscous, oily material.

The product, obtained after vacuum distillation, was a colorless oil, b.p. 90°C./0.03 mm., n_D^{20} 1.4722. Yield: 14.6 g. (70%).

Anal. Calcd. for $C_8H_{20}N_2O_2S$: C, 49.09; H, 9.15; N, 12.72.

Found : C, 48.77; H, 8.83; N, 12.84.

9. N,N-diethyl-N'-cyclohexyl-N'-methylsulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole), cyclohexylmethylamine (22.6 g., 0.2 moles), and 50 ml. of chloroform were placed in a flask equipped with a reflux condenser. Gentle heating was maintained for 1 hour while refluxing took place. The red solution was then distilled under vacuum in order to take off the excess of chloroform. After the removal of the solvent, the dark solid was washed with ether and filtered. The ether solution was then shaken with water in a separatory funnel and the ether layer dried over $CaCl_2$. The ether was distilled off, leaving a viscous, oily residue.

The product, obtained after two vacuum distillations, was a colorless oil, b.p. 101-102°C./0.2 mm., n_D^{24} 1.4726.

Anal. Calcd. for $C_{11}H_{24}N_2O_2S$: C, 53.21; H, 9.74; N, 11.28.

Found : C, 53.40; H, 9.78; N, 11.16.

10. N,N-diethyl-N'-phenyl-N'-methylsulfamide.-- Diethylsulfamylchloride (17.1 g., 0.1 mole) and methylaniline (21.6 g., 0.2 moles) were placed in a flask fitted with a condenser without solvent. Gentle heating was required to start the reaction, but then it carried on at room temperature. The mixture was left standing for 1 hour. The solid was dissolved in ether and filtered. The ether layer was dried over $CaCl_2$ and the ether distilled off leaving a yellow viscous oily residue.

The product, obtained after two vacuum distillation, was a colorless oil, b.p. 98°C./0.1 mm., n_D^{25} 1.5160.

Anal. Calcd. for $C_{11}H_{18}N_2O_2S$: C, 54.55; H, 7.49; N, 11.56.

Found: C, 54.32; H, 7.16; N, 11.35.

11. Attempted Preparation of Diphenylsulfamylchloride.-- Sulfuryl chloride (30 ml.) and 50 ml. of benzene were placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small separatory funnel. The flask was surrounded with an ice-water bath. Diphenylamine (16.9 g., 0.1 mole), dissolved in 50 ml. of benzene, was slowly added to the sulfuryl chloride with vigorous agitation. The mixture was warmed and poured into a 500 ml. flask and refluxed gently for 12 hours. It was then left standing overnight. The precipitate which was formed and crystallized from benzene.

The white compound, after two recrystallizations from n-heptane melts at 138-139°C., but it contains no sulfur. However, the chlorination product 2,4,6,2',2',6' hexachlorodiphenylamine is reported in Beilstein as having a m.p. of 138-139°C.

Anal. Calcd. for $C_{12}H_5Cl_6N$: C, 38.34; H, 1.34; N, 3.72.

Found : C, 38.47; H, 1.51; N, 4.19.

E. Discussion

Synthesis of tri- and tetrasubstituted sulfamides via reaction of N,N-disubstituted sulfamyl chlorides with primary and secondary amines presents no difficulty when the amines are reasonably strongly basic. However, reduction in basicity, as by excessive substitution with aryl groups limits the reaction. It will be profitable, of course, to check this generalization by use of additional amines of varying basicity. It is apparent that the products are obtainable in high purity with a minimum of experimental difficulty.

The compounds characterized are relatively high-boiling substances. They appear to be stable in air at ordinary temperatures, but data have not yet been obtained to indicate their thermal stabilities. That they are insoluble in water but soluble in organic solvents is an indication of both their high degree of covalency and their general organic natures.

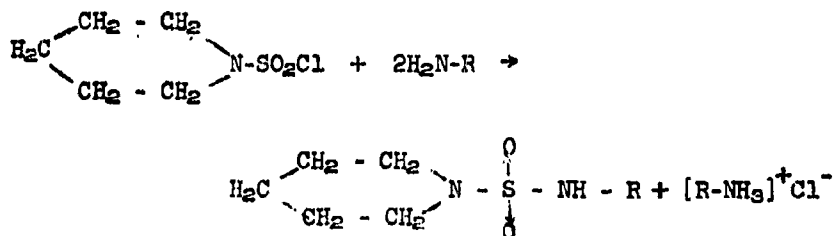
IV. Synthesis and Properties of N-Substituted Sulfamides

A. Introduction

With the object of preparing new N,N,N'-trisubstituted and N,N,N',N'-tetrasubstituted sulfamides in which the diethyl radical was replaced by an heterocyclic group, reactions of N-cyclopentamethylenesulfamyl chloride with different aliphatic and aromatic amines have been carried out during this synthesis program.

For this purpose N-cyclopentamethylenesulfamyl chloride has been prepared by the standard procedure (11) as modified by Audrieth and von Brauchitsch (12). During this investigation, ten N-substituted sulfamides all of new composition of matter not reported in the literature, have been prepared and characterized.

The general reaction with primary amines is represented by the following equation:



Where: R = H, C₆H₁₁-, 2-C₁₀H₇-, C₆H₅-, C₆H₅CH₂-,

p-CH₃C₆H₄-, o-CH₃C₆H₄-, m-CH₃C₆H₄-.

However when secondary or heterocyclic amines are employed the reaction

Table III
Analyses of Tri- and Tetrasubstituted Sulfamides

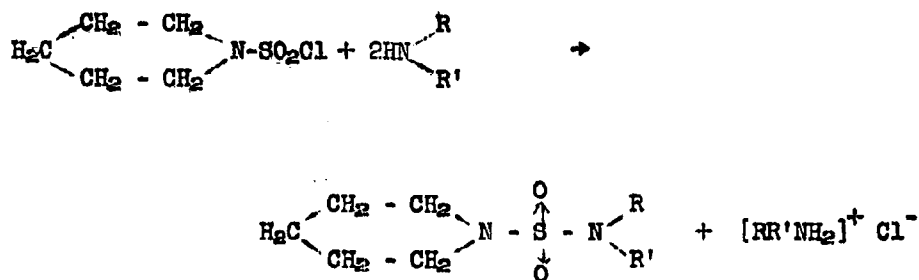
| <u>Compound</u> | <u>Empirical Formula</u> | <u>Carbon %</u> | | <u>Hydrogen %</u> | | <u>Nitrogen %</u> | |
|--|---|-----------------|--------------|-------------------|--------------|-------------------|--------------|
| | | <u>Calcd.</u> | <u>Found</u> | <u>Calcd.</u> | <u>Found</u> | <u>Calcd.</u> | <u>Found</u> |
| N,N-diethylsulfamide | C ₄ H ₁₂ N ₂ O ₂ S | 31.57 | 31.49 | 7.95 | 7.72 | 18.41 | 18.49 |
| N,N-diethyl-N'-butylsulfamide | C ₈ H ₂₀ N ₂ O ₂ S | 46.16 | 45.90 | 9.68 | 9.48 | 13.45 | 13.14 |
| N,N-diethyl-N'-cyclohexylsulfamide | C ₁₀ H ₂₂ N ₂ O ₂ S | 51.28 | 50.80 | 9.47 | 9.40 | 11.95 | 11.85 |
| N,N-diethyl-N'-phenylsulfamide | C ₁₀ H ₁₆ N ₂ O ₂ S | 52.64 | 52.48 | 7.06 | 7.11 | 12.28 | 11.95 |
| N,N-diethyl-N',N'-dibutylsulfamide | C ₁₂ H ₂₈ N ₂ O ₂ S | 54.53 | 54.35 | 10.68 | 10.34 | 10.60 | 10.31 |
| N,N-diethyl-4-morpholinesulfamide | C ₈ H ₁₆ N ₂ O ₃ S | 43.24 | 43.13 | 8.16 | 8.25 | 12.61 | 12.44 |
| N,N-diethyl-4-piperidinesulfamide | C ₉ H ₂₀ N ₂ O ₂ S | 49.09 | 48.77 | 9.15 | 8.83 | 12.72 | 12.84 |
| N,N-diethyl-N'-cyclohexyl-N'-methylsulfamide | C ₁₁ H ₂₄ N ₂ O ₂ S | 53.21 | 53.40 | 9.74 | 9.78 | 11.28 | 11.16 |
| N,N-diethyl-N'-phenyl-N'-methylsulfamide | C ₁₁ H ₁₈ N ₂ O ₂ S | 54.55 | 54.32 | 7.49 | 7.16 | 11.56 | 11.35 |

Table IV

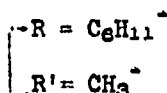
Properties of Tri- and Tetrasubstituted Sulfamides

| <u>Compound</u> | <u>M.P.</u> <u>(°C.)</u> | <u>B.P.</u> <u>(°C./mm.)</u> | <u>n_D^{t°C.}</u> |
|--|-----------------------------|---------------------------------|-------------------------------------|
| N,N-diethylsulfamide | 44 | --- | --- |
| N,N-diethyl-N'-phenylsulfamide | -- | 171/2.5 | 1.5260 |
| N,N-diethyl-N',N'-dibutylsulfamide | -- | 88/0.15 | 1.4500 |
| N,N-diethyl-N'-cyclohexylsulfamide | 49 | 136/1.0 | --- |
| N,N-diethyl-4-morpholine-sulfamide | -- | 91/0.15 | 1.4695 |
| N,N-diethyl-4-piperidine-sulfamide | -- | 90/0.03 | 1.4722 |
| N,N-diethyl-N'-cyclohexyl-N'-methylsulfamide | -- | 101-102/0.2 | 1.4726 |
| N,N-diethyl-N'-phenyl-N'-methylsulfamide | -- | 98/0.1 | 1.5160 |
| N,N-diethyl-N'-butylsulfamide | -- | 87/0.1 | 1.4510 |

proceeds as follows:



Where: R = R' is an heterocyclic group such as morpholine



The following N-substituted sulfamides were prepared by this type of reaction:

- I. N-cyclopentamethylenesulfamide
- II. N-cyclopentamethylene-N'cyclohexylsulfamide
- III. N-cyclopentamethylene-N'-2-naphthylsulfamide
- IV. N-cyclopentamethylene-N'-phenylsulfamide
- V. N-cyclopentamethylene-N'benzylsulfamide
- VI. N-cyclopentamethylene-N'-p-tolylsulfamide
- VII. N-cyclopentamethylene-N'-o-tolylsulfamide
- VIII. N-cyclopentamethylene-N'm-tolylsulfamide
- IX. N-cyclopentamethylene-4-morpholinesulfamide
- X. N-cyclopentamethylene-N'methyl-N'cyclohexylsulfamide

All of these compounds, except N-cyclopentamethylenesulfamide, were prepared in this way. N-cyclopentamethylenesulfamide was prepared by adding dropwise the pure cyclopentamethylenesulfamyl chloride to an excess of liquid ammonia with vigorous agitation over a period of 2 hours. After evaporation of the excess of liquid ammonia at room temperature, the pure product was obtained by recrystallization from normal heptane.

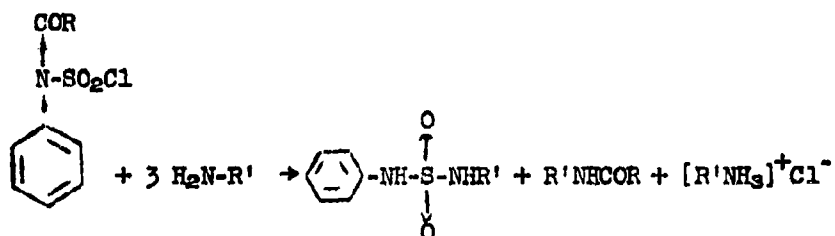
B. Physical Properties

Tri- and tetrasubstituted sulfamides are all white, crystalline materials, except N-cyclopentamethylene-N'methyl-N'cyclohexylsulfamide, which is a colorless oil. They are fairly soluble in the gamut of organic

organic solvents, slightly soluble in boiling water, and insoluble in cold water. Normal heptane and ether were found to be the best solvents for their recrystallization.

C. Attempted Preparation of Unsymmetrically Disubstituted Sulfamides

The reaction of aryl-acysulfamyl chlorides with ammonia and amines is reported in the literature as a general method for the preparation of organic sulfamides (13,14,15). According to these authors, mixtures in the molar ratio 1:3 were refluxed over a period of time, in benzene as a solvent, to yield the corresponding sulfamides as shown below:



As a matter of fact, not a great deal of experimental work has been described that would give a satisfactory explanation of the suggested procedure. In fact only three reactions, e.g. with ammonia, diethylamine and aniline, have been performed. The corresponding sulfamides were obtained.

Since no reactions with primary aliphatic amines are reported, we found it interesting to carry out some as a possible approach to obtain unsymmetrically disubstituted sulfamides. For this purpose we prepared phenylacetylsulfamyl chloride (16) and then allowed the latter to reflux in benzene over a period of time with butylamine in the molar ratio 1:3. The reaction takes place easily and after the removal of the hydrochloride the compound, which was recovered after recrystallization from ether, melted at 125°C. This corresponds to the melting point of the symmetrical disubstituted sulfamide, e.g. *N,N'*-dibutylsulfamide, and microanalytical data agree for such a compound.

Thus far, no further reactions have been carried out, but it seems reasonable to assume that the behavior of primary aliphatic amines may not be the same as that followed by ammonia, secondary amines, or aniline itself.

D. Experimental

The tri- and tetrasubstituted sulfamides synthesized were prepared by allowing cyclopentamethylenesulfamylchloride (1 mole) to react with a primary or secondary amine (2 moles) and refluxing in benzene as solvent. In any case an excess of amine, to react with the hydrogen chloride released, was usually used as acid acceptor. Numerical and analytical data for the compounds prepared are summarized in Table V.

Table V
Properties and Analyses of Tri- and Tetra-substituted Sulfamides

| Compound | Empirical Formula | M.P. B.P. (°C.) (°C./mm) | t°C n _D | Carbon % | | Hydrogen % | | Nitrogen % | |
|---|---|-----------------------------|-----------------------|----------|-------|------------|-------|------------|-------|
| | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -cyclohexylsulfamide | C ₁₁ H ₂₂ N ₂ O ₂ S | 75 -- | -- | 53.64 | 53.62 | 9.00 | 8.99 | 11.37 | 11.26 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -2'-naphthylsulfamide | C ₁₅ H ₁₈ N ₂ O ₂ S | 115-6 -- | -- | 62.05 | 61.81 | 6.25 | 6.32 | 9.65 | 9.63 |
| <u>N</u> -cyclopentamethylenesulfamide C ₅ H ₁₂ N ₂ O ₂ S | C ₅ H ₁₂ N ₂ O ₂ S | 120 -- | -- | 36.57 | 36.82 | 7.36 | 7.31 | 17.06 | 16.88 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -phenylsulfamide | C ₁₁ H ₁₆ N ₂ O ₂ S | 83 -- | -- | 54.98 | 55.18 | 6.71 | 6.69 | 11.66 | 11.39 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -benzylsulfamide | C ₁₂ H ₁₈ N ₂ O ₂ S | 100-1 -- | -- | 56.67 | 56.71 | 7.13 | 7.33 | 11.02 | 11.00 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -p-tolylsulfamide | C ₁₂ H ₁₈ N ₂ O ₂ S | 97-8 -- | -- | 56.67 | 56.91 | 7.13 | 7.20 | 11.02 | 10.94 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> -methyl- <u>N'</u> -cyclohexyl- sulfamide | C ₁₂ H ₂₄ N ₂ O ₂ S | -- 134/0.5 | 1.4970 | 55.34 | 55.11 | 9.29 | 9.20 | 10.75 | 10.46 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> - <u>m</u> -tolylsulfamide | C ₁₂ H ₁₈ N ₂ O ₂ S | 123-4 -- | -- | 56.67 | 56.83 | 7.13 | 7.15 | 11.02 | 10.74 |
| <u>N</u> -cyclopentamethylene- <u>N'</u> - <u>o</u> -tolylsulfamide | C ₁₂ H ₁₈ N ₂ O ₂ S | 94 -- | -- | 56.67 | 56.87 | 7.13 | 7.11 | 11.02 | 10.74 |
| <u>N</u> -cyclopentamethylene- <u>h</u> -morpholinesulfamide | C ₉ H ₁₈ N ₂ O ₃ S | 71-2 -- | -- | 46.14 | 46.27 | 7.74 | 7.70 | 11.96 | 11.99 |

1. Cyclopentamethylenesulfamylchloride. - To a solution of 70 g. of sulfurylchloride (0.5 mole) in 150 ml. of toluene, cooled in an ice-salt bath, there were added dropwise with vigorous agitation 85 g. of piperidine (1.0 mole) at such a rate that the temperature of the reaction mixture was maintained below 0°C. Then 25 ml. of water was added and the mixture was allowed to warm at room temperature. The toluene layer was separated from the aqueous layer and was washed successively with water, with 10% hydrochloric acid to remove unreacted piperidine, with sodium bicarbonate solution, and finally again with water. The solution was then dried over Na_2SO_4 . The excess of toluene was first removed by distillation and the residue was fractionated under reduced pressure yielding a colorless oil, b.p. 95°C/1 mm. Yield 40.0 g. (40.0%).

Anal. Calcd. for $\text{C}_5\text{H}_{10}\text{NSO}_2\text{Cl}$: C, 32.71; H, 5.49; N, 7.63

Found: C, 32.96; H, 5.55; N, 7.78

2. N-cyclopentamethylene-N'-cyclohexylsulfamide. - Cyclopentamethylenesulfamylchloride (9.175 g., 0.05 mole), cyclohexylamine (9.9 g., 0.1 mole), and 50 ml. of benzene were placed in a flask equipped with a reflux condenser. Gentle refluxing was maintained for 6 hours. The hydrochloride was removed by filtration and washed with ether. The excess of solvent was then distilled off, leaving a white residue which was recrystallized twice from n-heptane. The pure compound was a white, crystalline material, melting at 75°C. Yield 8.2 g. (65.0%).

Anal. Calcd. for $\text{C}_{11}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$: C, 53.64; H, 9.00; N, 11.37

Found : C, 53.62; H, 8.99; N, 11.26

3. N-cyclopentamethylene-N'-2-naphthylsulfamide. - 2-Naphthylamine (14.31 g., 0.1 mole) dissolved in 50 ml. of benzene and cyclopentamethylene-sulfamylchloride (9.175 g., 0.05 mole) were placed in a flask fitted with a reflux condenser. Gentle refluxing was maintained for 12 hours. The hydrochloride was removed by filtration and washed with ether. The organic layer distilled off leaving a brown residue. This was dissolved in boiling ether from which on cooling a white material with melting point 115-116°C. crystallized. Yield 3.0 g. (20.0%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 62.05; H, 6.25; N, 9.65

Found : C, 61.81; H, 6.32; N, 9.63

4. N-cyclopentamethylenesulfamide. - Liquid ammonia (100 ml.) was placed in a three-necked flask fitted with a mechanical stirrer, an outlet tube and a small separatory funnel. The flask was surrounded with a bath of methylcellosolve and "dry-ice" to keep the temperature at -70°C. Cyclopentamethylenesulfamylchloride (9.175 g., 0.05 mole) was added dropwise over a two-hour period with vigorous agitation. The solution was stirred for two additional hours, and then the flask was kept at room temperature to allow evaporation of the excess of liquid ammonia. The mixture was treated with hot ether and filtered in order to remove the ammonium chloride. Upon cooling a white material

was recovered which, after recrystallization from ether, melted at 120°C. Yield 4.5 g. (55.0%).

Anal. Calcd. for $C_5H_{12}N_2O_2S$: C, 36.57; H, 7.36; N, 17.06

Found: C, 36.82; H, 7.31; N, 16.88

5. N-cyclopentamethylene-N'-phenylsulfamide. - Cyclopentamethylene-sulfamylchloride (9.175 g., 0.05 mole), aniline (9.3 g., 0.1 mole), and 50 ml. of benzene were placed in a flask equipped with a reflux condenser. The mixture was allowed to reflux for 12 hours, after which time it was filtered to remove the hydrochloride. It was washed with ether and the organic layer distilled off, leaving a dark residue. After two recrystallizations from *n*-heptane, a white, crystalline compound was obtained, giving a sharp melting point at 83°C.

Anal. Calcd. for $C_{11}H_{16}N_2O_2S$: C, 54.98; H, 6.71; N, 11.66

Found : C, 55.18; H, 6.69; N, 11.39

6. N-cyclopentamethylene-N'-benzylsulfamide. - To 10.71 g. (0.1 mole) of benzylamine in 50 ml. of benzene, 9.175 g. (0.05 mole) of cyclopentamethylene-sulfamylchloride were added, and the mixture was refluxed gently for 6 hours. The hydrochloride was separated by filtration and washed with ether. The excess of organic solvent was distilled off leaving an organic residue which, after recrystallization first from *n*-heptane and successively from ether, gave a white, crystalline material with melting point 100-101°C. Yield 5.3 g. (42.0%).

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.02

Found : C, 56.71; H, 7.33; N, 11.00

7. N-cyclopentamethylene-N'-p-tolylsulfamide. - *p*-Toluidine (10.71 g., 0.1 mole), dissolved in 50 ml. of benzene, and cyclopentamethylenesulfamylchloride (9.175 g., 0.05 mole) were placed in a flask fitted with a reflux condenser. Gentle heating was continued for 6 hours. The hydrochloride was removed by filtration and washed with ether. The organic layer was distilled off, leaving a brown residue which was recrystallized twice from *n*-heptane. The pure compound was a white, crystalline material which melted at 97-98°C. Yield 7.0 g. (55.0%)

Anal. Calcd. for $C_{12}H_{18}N_2O_2S$: C, 56.67; H, 7.13; N, 11.02

Found: C, 56.91; H, 7.20; N, 10.94.

8. N-cyclopentamethylene-N'-methyl-N'-cyclohexylsulfamide. Cyclopentamethylenesulfamylchloride (9.175 g., 0.05 mole), methylcyclohexylamine (11.32 g., 0.1 mole), and 50 ml. of benzene were placed in a flask equipped with a reflux condenser. Gentle refluxing was maintained for 12 hours. The hydrochloride was removed by filtration and washed with ether. The organic layer was then distilled off, leaving a viscous oil which was partitioned between water and ether and shaken in a separatory funnel. The ether layer

was dried over calcium chloride and the ether distilled off, leaving an oily material. The product, obtained after vacuum distillation, was a colorless, viscous oil, b.p. $134^{\circ}\text{C}/0.5\text{ mm}$, n_D^{22} 1.4970. Yield 6 g. (45.0%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$: C, 55.34; H, 9.29; N, 10.75.

Found: C, 55.11; H, 9.20; N, 10.45.

9. N-cyclopentamethylene-N'-m-tolylsulfamide. - Cyclopentamethylene-sulfamylchloride (9.175 g., 0.05 mole), m-toluidine (10.71 g., 0.1 mole), and 50 ml. of benzene were mixed together in a flask fitted with a reflux condenser and gentle refluxing was maintained for 12 hours. The hydrochloride was separated by filtration and washed with ether. The organic layer was then distilled off yielding a brown residue which after two recrystallizations from carbon tetrachloride gave a white, crystalline material melting at $123\text{--}124^{\circ}\text{C}$. Yield 9.0 g. (70.0%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 56.67; H, 7.13; N, 11.02.

Found : C, 56.83; H, 7.15; N, 10.74.

10. N-cyclopentamethylene-N-o-tolylsulfamide. - Cyclopentamethylene-sulfamylchloride (9.175 g., 0.05 mole) and o-toluidine (10.71 g., 0.1 mole) were mixed together without solvent in a flask equipped with a reflux condenser. Gentle heating was required to start the reaction, but then it continued at room temperature. The mixture was left standing for 2 hours. The solid obtained was dissolved in ether and the hydrochloride removed by filtration. The ether layer was then distilled off leaving a brown residue which, after recrystallization from n-heptane, turned into a white, crystalline compound that melted at 94°C . Yield 8 g. (62.0%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 56.67; H, 7.13; N, 11.02

Found : C, 56.87; H, 7.11; N, 10.74

11. N-cyclopentamethylene-4-morpholinesulfamide. - Cyclopentamethylene-sulfamylchloride (9.175 g., 0.05 mole), morpholine (8.71 g., 0.1 mole), and 50 ml. of benzene were placed in a flask fitted with a reflux condenser. The reaction is very exothermic and no heat was necessary at the beginning. Then gentle heating was continued for 6 hours. The hydrochloride was removed by filtration and washed with ether. The organic layer was then distilled off leaving a brown residue which, after recrystallization from n-heptane, turned into a white crystalline compound with melting point $71\text{--}72^{\circ}\text{C}$. Yield 9.5 g. (81.0%).

Anal. Calcd. for $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_3\text{S}$: C, 46.14; H, 7.74; N, 11.96

Found: C, 46.27; H, 7.70; N, 11.99

12. Phenylacetylsulfamyl chloride. - To a suspension of 25.987 g. (0.15 mole) of potassium acetoanilide in 400 ml. of dry toluene (previously prepared by refluxing for 12 hours a solution of 20.27 g. (0.15 mole) of the amide in toluene with 5.86 g. (0.15 mole) of finely divided alkali metal) 20.20 g. (0.15 mole) of sulfuryl chloride in 150 ml. of toluene was added dropwise

with vigorous agitation at such a rate that the temperature could be maintained at -5°C . by cooling the reaction flask with an ice-salt bath. The flask was then allowed to warm at room temperature, and stirring was continued for 2 hours. The potassium chloride was separated by means of filtration, and the excess of toluene was distilled off under reduced pressure. A brown solid material was left which, after two recrystallizations from absolute alcohol, yielded a white, needle-shaped compound which melted at $75-76^{\circ}\text{C}$. Yield 11.0 g. (33%).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{NO}_3\text{ClS}$: C, 41.14; H, 3.45; N, 5.99

Found: C, 41.20; H, 3.62; N, 6.03.

13. Attempted Preparation of N-phenyl-N'-butylsulfamide. Phenylacetysulfamyl chloride (4.66 g., 0.02 mole), butylamine (4.38 g., 0.06 mole), and 50 ml. of benzene were mixed together in a flask fitted with a reflux condenser. Gentle heating was continued for 6 hours. The hydrochloride was removed by filtration and washed with ether. The organic layer was distilled off under vacuum and a brown, viscous oily material was left. Upon being treated with water, a white crystalline compound was separated, which, after recrystallization from ether, melted at 125°C . This corresponds to the melting point of N,N'-di-butylsulfamide.

Anal. Calcd. for $\text{C}_8\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 46.55; H, 9.68; N, 13.46

Found : C, 46.38; H, 9.89; N, 13.36

V. Thermal Characteristics of Tri- and Tetra-Substituted Sulfamide

A. Liquid Range

Theoretically, the liquid range of a compound should be given by the difference between the mid-point of the melting range and the mid-point of the boiling range at one atmosphere of pressure. Unfortunately, it has been impossible to apply such a criterion exactly to the N-substituted sulfamides previously described because all of these compounds decompose before boiling at normal pressure. Consequently, it has been feasible only to estimate an approximate liquid range by subtracting the mid-point of the melting range from the mid-point of the decomposition range.

Melting (freezing) points were determined by the cooling curve method. Volatilization (decomposition) ranges were determined by the method of Siwoloboff (17). Experimental data, in terms of uncorrected temperatures, are given in Table VI and VII.

B. Thermal Stability

The thermal stability of a compound may be defined as the resistance of the compound to decomposition brought about solely by thermal energy. Methods of evaluating this property are purely empirical and must refer quite arbitrarily to some selected standards of stability and temperature. The method used here was designed for the rapid screening of compounds (18).

It is based upon the observation that the thermal degradation of most compounds involves the elimination of one or more volatile fragments. The procedure amounts to determining the weight loss of the compound in question after heating in an inert atmosphere for a specified time at a specified temperature. For screening purposes in this study, 0.2-0.4 g. of the sample was heated under nitrogen at 10 mm. positive pressure at 200°C. (392°F.) for a period of 10 hours, and the weight loss was determined.

The apparatus used was a relatively simple thermal balance, constructed according to the suggestions of Winslow and Matyerik (19). One pan of a semi-micro balance is replaced by a platinum wire, to the other end of which a Pyrex sample container is attached. The latter is contained in a glass cell to which nitrogen can be admitted and which can be heated. The weight loss is then followed continuously without interrupting the heating.

Experimental data are summarized, in order of increasing thermal stability, in Tables VI and VII. All of the compounds that showed a weight loss less than 3.0% after 10 hours at 392°F. have been classified arbitrarily as thermally stable. Those showing a greater weight loss have been termed thermally unstable.

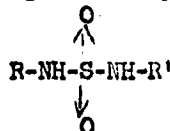
C. Discussion

In terms of these criteria, none of the compounds listed in Table I and Table II is thermally stable. Although the weight loss in each instance may be due in part to the loss of sorbed moisture, the total loss in each case is too large for this alone, suggesting that actual decomposition has occurred. This is supported by the observation that when N,N-diethyl-N',N'-dibutylsulfamide was heated at 250°C. for 10 hours, the loss in weight increased to 35.1%. It is to be noted that all of these compounds contain two ethyl groups or a cyclopentamethylene radical. Of the other groups present, the butyl and phenyl radicals are well known for their thermal stabilities. Compounds containing these have somewhat enhanced stabilities, but no profound differences are noted. It is reasonable to conclude, therefore, that the observed thermal instability is due to the ethyl and cyclopentamethylene radicals.

VI. Synthesis and Properties of N,N'-Disubstituted Sulfamides.

A. Introduction

The importance of preparing and studying unsymmetrical sulfamides of the type



where R and R' are different alkyl or aryl groups, has been emphasized previously. Although much work has been reported on the symmetrically disubstituted compounds, RNHSO₂NHR, no unsymmetrical compounds have been described.

Table VI
Properties of Tri- and Tetra- Substituted Sulfamides

| <u>Compound</u> | <u>Approximate liquid range, °C.</u> | <u>Weight loss after 10 hrs at 392°F. (%)</u> |
|--|--|---|
| N,N-diethyl-N',N'-dibutylsulfamide | * | 3.88 |
| N,N-diethyl-4-piperidinesulfamide | 268 | 4.51 |
| N,N-diethyl-N'-phenylsulfamide | 247 | 4.72 |
| N,N-diethyl-N'-cyclohexyl-N'-methylsulfamide | 354 | 6.20 |
| N,N-diethyl-N'-cyclohexylsulfamide | 273 | 6.63 |
| N,N-diethyl-4-morpholinesulfamide | * | 7.85 |
| N,N-diethyl-N'-butylsulfamide | 276 | 7.91 |
| N,N-diethyl-N'-methyl-N'-phenylsulfamide | 263 | 8.72 |
| N,N-diethylsulfamide | 234 | 12.00 |

* No freezing point was observed at -75°C.

Table VII

Properties of N-Substituted Sulfamides

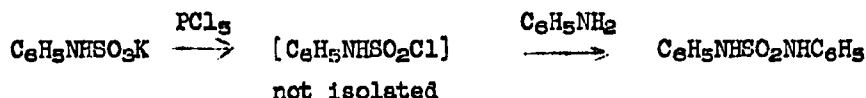
| <u>Compound</u> | <u>Approximate Liquid range, °C</u> | <u>Weight loss after 10 hrs. at 392°F (2)</u> |
|--|---|---|
| <u>N</u> -cyclopentamethylene-4-morpholinesulfamide | 170 | 4.13 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-methyl- <u>N</u> '-cyclohexylsulfamide * | | 7.66 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-2 naphthylsulfamide | 118 | 16.33 |
| <u>N</u> -cyclopentamethylenesulfamide | 80 | 41.28 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-benzylsulfamide | 122 | 42.80 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-phenylsulfamide | 150 | 43.23 |
| <u>N,N</u> '-diamylsulfamide | 117 | 46.56 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-m-tolylsulfamide | 100 | 46.57 |
| <u>N,N</u> '-dibutylsulfamide | 126 | 48.70 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-cyclohexylsulfamide | 167 | 51.57 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-p-tolylsulfamide | 135 | 56.98 |
| <u>N,N</u> '-dipropylsulfamide | 121 | 57.93 |
| <u>N</u> -cyclopentamethylene- <u>N</u> '-o-tolylsulfamide | 139 | 65.30 |

*No freezing point was observed at -75°C.

The symmetrical compounds are easily produced either by reactions between sulfuryl chloride and amines at low temperatures in the presence of an inert solvent (20) or by deamination reactions of sulfamide with primary aliphatic and aromatic amines. The synthesis of the unsymmetrical substances, on the other hand, requires the monoalkyl (aryl) sulfamyl chlorides, RNHSO_2Cl , as starting materials.

Attempts to prepare mono-substituted sulfamyl chlorides have been generally unproductive. Secondary amines, either as such or as hydrochlorides, react readily with sulfuryl chloride to yield N,N-disubstituted sulfamyl chlorides, but primary amines do not behave in this fashion. Thus, refluxing ethylaminehydrochloride with excess sulfuryl chloride for 48 hours, either in the presence of an inert solvent or in its absence, yields unreacted ethylaminehydrochloride. On the other hand, treating a dilute solution of sulfuryl chloride in an inert diluent with a primary amine in the same diluent yields the symmetrical compound RNHSO_2RNH and aminehydrochloride as principal products.

A survey of the literature reveals a number of attempts to synthesize pure monoalkyl (aryl) sulfamyl chlorides. Although such compounds have been postulated as intermediates, none has ever been isolated as such, and the methods yield RNHSO_2NHR -type compounds. Similarly, Traube (21), by treating potassium N-phenyl sulfamate with phosphorus(V) chloride, apparently obtained the sulfamyl chloride only as an intermediate as

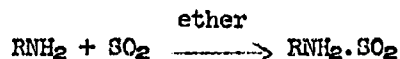


Recently, it has been reported (22) that when a dialkylamidodisulfonic acid is treated with a stream of chlorine over a period of time, pure N,N-dialkylsulfamyl chlorides result in satisfactory yields.



Since as no data were given for monoalkylamido compounds, it has been of interest to investigate this procedure as a possible approach to monoalkyl (aryl) sulfamyl chlorides.

It is well known (23) that primary aliphatic and aromatic amines react with sulfur dioxide under anhydrous conditions and in an inert solvent to yield adducts, as



where R=alkyl or aryl group. If chlorine is passed through such a mixture at room temperature for a period of time, an exothermic reaction occurs, and N,N'-disubstituted sulfamides result. Although the initial purpose of isolating N-substituted sulfamyl chlorides, was not realized, this reaction has given a new approach to the preparation of the symmetrical sulfamides and has obviated the use of sulfuryl chloride.

It is reasonable to assume that the reaction involved takes place in the following steps



where $\text{R}=\text{R}'=\text{C}_3\text{H}_7$, C_4H_9 , C_5H_{11} , C_6H_{11} , $\text{C}_6\text{H}_5\text{CH}_2$. The following compounds have been prepared by this means:

- I. N,N'-di-n-propylsulfamide
- II. N,N'-di-n-butylsulfamide
- III. N,N'-di-t-butylsulfamide
- IV. N,N'-di-n-amylsulfamide
- V. N,N'-dicyclohexylsulfamide
- VI. N,N'-dibenzylsulfamide

Aliphatic amines react readily, with reactivity increasing with increasing basic strength. Aromatic amines such as aniline and p-toluidine are oxidized by chlorine to uncharacterized red products but yield no sulfamides. However, benzylamine reacts smoothly to give, in low yield, a white, crystalline product, agreeing in melting point (181-182°C.) with that listed for N,N'-dibenzylsulfamide (24).

B. Chemical and Physical Properties

The symmetrical disubstituted sulfamides are white, crystalline compounds, that are soluble in all the common organic solvents, quite insoluble in cold water, and only slightly soluble in boiling water. They are best recrystallized from carbon tetrachloride or benzene. Melting point and analytical data are summarized in Table VIII.

Because of the presence of two acidic hydrogen atoms, they dissolve readily in aqueous alkali, yielding the corresponding alkali metal salts.

C. Experimental

The amine-sulfur dioxide adducts were obtained by treating 0.05-mole quantities of the amines in ether solution with sulfur dioxide at 0°C. for 1-hour periods. The symmetrical disubstituted sulfamides were obtained by treating 0.05 mole quantities of these adducts in ether solution with chlorine gas for 2-hour periods at room temperature.

1. N,N'-di-n-propylsulfamide. Two and ninety-five hundredths grams (0.05 mole) of n-propylamine dissolved in 100 ml. of anhydrous ether was placed in a 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and an inlet tube for sulfur dioxide or chlorine. The solution was cooled to 0°C. and stirred vigorously while sulfur dioxide was passed through it for a period of 1 hour. A white precipitate of the amine-sulfur dioxide adduct separated. The contents of the flask were allowed to warm to room temperature, and chlorine was passed through the suspension for a total of 2 hr., while an exothermic reaction took place.

Table VIII
Properties and Analyses of Disubstituted Sulfamides

| Compound | Empirical Formula | M. P. (°C) | Carbon % | | Hydrogen % | | Nitrogen % | |
|-----------------------------|-----------------------|---------------|----------|-------|------------|-------|------------|-------|
| | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| N,N'-di-n-propylsulfamide | $C_6H_{16}N_2O_2S$ | 118-119 | 39.99 | 39.92 | 8.95 | 8.65 | 15.55 | 15.45 |
| N,N'-di-n-butylsulfamide | $C_8H_{20}N_2O_2S$ | 125 | 46.15 | 46.55 | 9.68 | 9.65 | 13.46 | 13.33 |
| N,N'-di-t-butylsulfamide | $C_9H_{20}N_2O_2S$ | 142-143 | 46.15 | 46.51 | 9.68 | 9.78 | 13.46 | 13.22 |
| N,N'-di-n-amylysulfamide | $C_{10}H_{24}N_2O_2S$ | 127-128 | 50.82 | 50.92 | 10.24 | 10.39 | 11.85 | 11.89 |
| N,N'-di-cyclohexylsulfamide | $C_{12}H_{24}N_2O_2S$ | 152-153 | 55.37 | 55.54 | 9.29 | 9.06 | 10.76 | 10.61 |

The reaction mixture was then filtered and the precipitate washed with ether. The ether layer was concentrated under vacuum and then treated slowly with water to precipitate the disubstituted sulfamide. The filtered and dried crude product was purified by recrystallization from carbon tetrachloride. It was a white, crystalline compound, melting at 118-119°C.

Anal. Calcd. for $C_8H_{16}N_2O_2S$: C, 39.99; H, 8.95; N, 15.55

Found : C, 39.92; H, 8.65; N, 15.45.

2. N,N'-di-n-butylsulfamide. - Three and sixty-five hundredths grams (0.05 mole) of redistilled n-butylamine dissolved in 100 ml. of anhydrous ether was placed in a 3-necked flask fitted with a mechanical stirrer, a reflux condenser, and an inlet tube for sulfur dioxide or chlorine. Sulfur dioxide was then passed through the vigorously stirred solution at 0°C. for 1 hr., yielding a white, ether-insoluble adduct. The suspension was allowed to warm to room temperature and treated with chlorine for 2 hours.

The reaction mixture was filtered and the precipitate extracted with ether. The ether layer was concentrated under vacuum and treated with water to precipitate the crude product. The dried crude material was purified by recrystallization from carbon tetrachloride to a white crystalline solid melting at 125°C.

Anal. Calcd. for $C_8H_{20}N_2O_2S$: C, 46.15; H, 9.68; N, 13.46.

Found: C, 46.51; H, 9.78; N, 13.22.

3. N,N'-di-t-butylsulfamide. Three and sixty-five hundredths grams (0.05 mole) of redistilled t-butylamine dissolved in 100 ml. of anhydrous ether was placed in a flask equipped with a reflux condenser, a mechanical stirrer, and an inlet tube for sulfur dioxide or chlorine. Sulfur dioxide was then passed through the solution for 1 hr. at 0°C. with vigorous agitation. The resulting suspension was allowed to warm to room temperature and treated with chlorine for 2 hours.

The reaction mixture was filtered and the precipitate extracted with ether. The ether layer was concentrated under vacuum and treated with water. The precipitated material was recrystallized from carbon tetrachloride to a white crystalline solid melting at 142-143°C.

Anal. Calcd. for $C_8H_{20}N_2O_2S$: C, 46.15; H, 9.68; N, 13.46.

Found : C, 46.51; H, 9.78; N, 13.22

4. N,N'-di-n-amylsulfamide. - Four and thirty-five hundredths grams (0.05 mole) of n-amylamine dissolved in 100 ml. of anhydrous ether was placed in a 3-necked flask fitted with a reflux condenser, a mechanical stirrer, and an inlet tube for sulfur dioxide or chloride. Sulfur dioxide was passed through the vigorously stirred solution for 1 hr. at 0°C. Chlorine was then passed through the suspension for 2 hours at room temperature.

The reaction mixture was filtered and the solid extracted with ether. The ether layer was concentrated under vacuum and treated with water. The precipitated substituted sulfamide was dried and recrystallized from carbon tetrachloride to a white, crystalline solid melting at 127-128°C.

Anal. Calcd. for $C_{10}H_{24}N_2O_2S$: C, 50.82; H, 10.24; N, 11.85.

Found : C, 50.92; H, 10.39; N, 11.89.

5. N,N'-dicyclohexylsulfamide. - Four and ninety-five hundredths gram (0.05 mole) of cyclohexylamine dissolved in 100 ml. of anhydrous ether was placed in a 3-necked flask equipped with a mechanical stirrer, a reflux condenser, and an inlet tube for sulfur dioxide or chlorine. The vigorously stirred solution was treated with sulfur dioxide at 0°C. for 1 hr. The resulting suspension was then chlorinated at room temperature for 8 hours.

The reaction mixture was filtered and the precipitate extracted with ether. The ether layer was concentrated under vacuum to a volume of only a few milliliters and treated slowly with water with vigorous stirring. The crude substituted sulfamide was recrystallized from carbon tetrachloride to a white, crystalline substance melting at 152-153°C.

Anal. Calcd. for $C_{12}H_{24}N_2O_2S$: C, 55.37; H, 9.29; N, 10.76.

Found: C, 55.54; H, 9.06; N, 10.61

VII. Reactions of Dialkylsulfamyl Chlorides with Polyamines.

A. Introduction

Aminolysis of dialkylsulfamyl chlorides with aliphatic, aromatic, and heterocyclic amines to produce organic sulfamides, is described in the literature. Recently it has been of interest to investigate in detail methods of synthesis and both chemical and physical properties for a number of such compounds. No reactions involving the use of polyamines have been thus far reported, however, we found it interesting therefore, to investigate several either to characterize this new class of compounds from a chemical point of view or to provide a possible approach to increasing their thermal stability.

Theoretically, on reacting dialkylsulfamyl chlorides with polyamines, sulfamylation might occur on one or both nitrogen atoms of the polyamine, leading consequently to mono- or di-substituted derivatives. During our investigation, it has been possible to synthesize twelve new di-substituted compounds, but even under proper conditions, no mono-substituted derivatives have been isolated. This suggests that perhaps sulfamylation occurs at the same rate on both nitrogen atoms of the polyamines employed.

These aminolytic reactions do not proceed as easily as in the case in which aliphatic or aromatic amines are employed; the yields, averaging

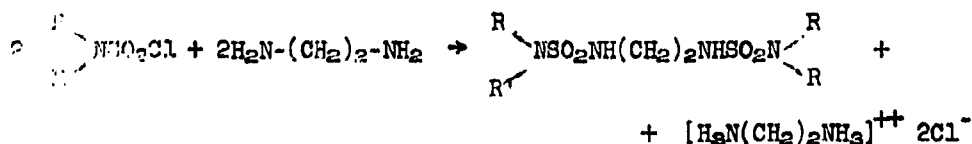
ca. 45%, are also lower. A reasonable explanation of these low yields may involve firstly the fact that polyamines are commonly not very soluble, and sometimes completely insoluble, in the organic solvents; consequently the reaction may not proceed in a stoichiometrical fashion. Secondly, the possibility that mono-substituted derivatives might be formed as by-products together with the desired products, even if they have not been isolated, cannot be excluded. Perhaps because of their extreme solubility their recovery has not been thus far possible.

Four dialkylsulfamyl chlorides, e.g. diethyl-, dimethyl-, n-cyclopentamethylene-, and n-morpholinesulfamyl chloride have been made to react with ethylenediamine, hexamethylenediamine, and piperazine, respectively. Thus far diethylenetriamine has been caused to react only with n-cyclopentamethylenesulfamyl chloride.

Because of problems of insolubility, a specific solvent is required for each reaction. Thus, reactions with ethylenediamine were carried out in ether as a solvent; with hexamethylenediamine chloroform was employed; and finally with piperazine alcohol was found to be the most suitable. The reactions are exothermic and very often are complete at room temperature over a period of time; in some cases gentle heating was required for their completion.

For synthesis purposes, diethyl- and n-cyclopentamethylenesulfamyl chloride were prepared in the same manner as mentioned previously (9,12); dimethylsulfamyl chloride was prepared by the standard procedure (25). N-morpholinesulfamyl chloride has never been prepared in this way. It was known as a product of the reaction between n-morpholine chloroamine and sulfur dioxide (22), but we preferred to synthesize the material by aminolysis of sulfuryl chloride. It is a colorless oil, which boils at 42°C. at 0.6 mm.

The general reaction with ethylenediamine is given as an example in the equation:



where:

R = R' may be CH₃⁻, C₂H₅⁻, C₅H₁₀ (from piperidine),
C₄H₈O (from morpholine)

Piperazine, hexamethylenediamine, and diethylenetriamine were employed as well.

The following compounds were prepared by this type of reaction:

- I. N,N'-bis(diethylsulfamido)ethylenediamine
- II. N,N'-bis(diethylsulfamido)hexamethylenediamine
- III. N,N'-bis(diethylsulfamido)piperazine

- IV. N,N'-bis(n-cyclopentamethylenesulfamido)ethylenediamine
- V. N,N'-bis(n-cyclopentamethylenesulfamido)hexamethylenediamine
- VI. N,N'-bis(n-cyclopentamethylenesulfamido)piperazine
- VII. N,N'-bis(n-morpholinesulfamido)ethylenediamine
- VIII. N,N'-bis(n-morpholinesulfamido)hexamethylenediamine
- IX. N,N'-bis(n-morpholinesulfamido)piperazine
- X. N,N'-bis(dimethylsulfamido)hexamethylenediamine
- XI. N,N'-bis(dimethylsulfamido)piperazine
- XII. N,N'-N''-tris(n-cyclopentamethylenesulfamido)diethylenetriamine

B. Physical Properties

The N-substituted sulfamides here synthesized are all white, crystalline materials. Their melting points are not sharp, and all sinter a few degrees before they melt. They are insoluble in cold water and sometimes slightly soluble in boiling water but not without decomposition. In regard to organic solvents, every compound behaves in a particular way, and to find a general rule is quite impossible. Those compounds containing the piperazine molecule are completely insoluble, but fortunately they can be recovered from the reaction mixture in high purity. The remaining are fairly soluble in alcohol, chloroform, and sometimes also in ether and carbon tetrachloride. All are insoluble in n-heptane and petroleum ether. Alcohol, carbon tetrachloride, and ether were found to be the best solvents for their recrystallization.

C. Thermal Stability and Liquid Range

It has been emphasized previously that for screening purposes we may classify arbitrarily as thermally stable all those compounds which show a weight loss less than 3.0%, when heated at a specified temperature for a period of 10 hours. According to this empirical criterion, among the compounds here synthesized, only three are to be considered arbitrarily as thermally stable at 200°C. (392°F.). However, when the temperature was raised to 220°C. (428°F.), appreciable thermal decomposition seems to occur even with these since loss of weight increases rapidly.

Of the remaining compounds, even at 200°C., none can be classified as thermally stable inasmuch as thermal decomposition at that temperature occurs.

The liquid range and thermal stability values, in terms of uncorrected temperatures and of increasing weight loss, are listed in Table IX.

D. Experimental

All the compounds were prepared by mixing the two components in the molar ratio 1:1 in the appropriate solvent and leaving the mixture standing at room temperature for a period of time or refluxing gently when necessary. In any case an excess of polyamine was usually used as acid acceptor to remove the hydrogen chloride released. The yields were calculated on the basis of the dialkylsulfamyl chloride employed. Numerical and analytical data for the compounds prepared are summarized in Table X.

Table IX

Properties of N-Substituted Sulfamides

| <u>Compound</u> | <u>Approximate Liquid Range °C.</u> | <u>Weight Loss after 10 hrs. at 392°F. (%)</u> | <u>Weight Loss after 10 hrs. at 428°F. (%)</u> |
|---|---|--|--|
| <u>N,N'</u> -bis(morpholinesulfamido)piperazine | 12 | 0 | 4.40 |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethylenesulfamido)piperazine | 23 | 0.24 | 12.7 |
| <u>N,N'</u> -bis(dimethylsulfamido)piperazine | 39 | 0.92 | 18.8 |
| <u>N,N'</u> -bis(diethylsulfamido)piperazine | 133 | 6.65 | -- |
| <u>N,N'</u> -bis(diethylsulfamido) hexamethylenediamine | 148 | 53.6 | -- |
| <u>N,N'</u> -bis(dimethylsulfamido) hexamethylenediamine | 96 | 54.0 | -- |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethylenesulfamido) ethylenediamine | 92 | 60.0 | -- |
| <u>N,N'</u> -bis(<u>n</u> -morpholinesulfamido) hexamethylenediamine | 94 | 62.0 | -- |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethylenesulfamido) hexamethylenediamine | 110 | 65.0 | -- |
| <u>N,N',N''</u> -tris(<u>n</u> -cyclopentamethylenesulfamido) diethylenetriamine | 84 | 73.0 | -- |
| <u>N,N'</u> -bis(diethylsulfamido) ethylenediamine | 154 | 80.0 | -- |
| <u>N,N'</u> bis(<u>n</u> -morpholinesulfamido) ethylenediamine | 100 | 81.0 | -- |

Table X
Properties and Analyses of N-Substituted Sulfamides

| Compound | Empirical Formula | M.P. (°C.) | Carbon % | | Hydrogen % | | Nitrogen % | |
|---|-------------------------|---------------|----------|-------|------------|-------|------------|-------|
| | | | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| <u>N,N'</u> -bis(diethylsulfamido) ethylenediamine | $C_{10}H_{20}N_4O_4S_2$ | 52 | 36.35 | 36.36 | 7.93 | 7.76 | 16.96 | 16.73 |
| <u>N,N'</u> -bis(diethylsulfamido) hexamethylenediamine | $C_{14}H_{28}N_4O_4S_2$ | 65 | 43.50 | 43.24 | 8.86 | 8.52 | 14.50 | 14.36 |
| <u>N,N'</u> -bis(diethylsulfamido) | $C_{12}H_{24}N_4O_4S_2$ | 107-8 | 40.44 | 40.68 | 7.92 | 7.73 | 15.72 | 15.62 |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethyl- lenesulfamido) ethylenediamine | $C_{12}H_{20}N_4O_4S_2$ | 128-9 | 40.67 | 40.82 | 7.39 | 7.34 | 15.81 | 15.51 |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethyl- lenesulfamido) piperazine | $C_{14}H_{28}N_4O_4S_2$ | 241-2 | 44.19 | 44.36 | 7.42 | 7.26 | 14.73 | 14.92 |
| <u>N,N'</u> -bis(<u>n</u> -cyclopentamethyl- lenesulfamido) hexamethylenediamine | $C_{16}H_{32}N_4O_4S_2$ | 105-6 | 46.81 | 46.70 | 8.35 | 8.25 | 13.65 | 13.48 |
| <u>N,N'</u> -bis(<u>n</u> -morpholinesulfamido) ethylenediamine | $C_{10}H_{22}N_4O_6S_2$ | 130-1 | 33.51 | 33.65 | 6.18 | 6.06 | 15.63 | 15.63 |
| <u>N,N'</u> -bis(<u>n</u> -morpholinesulfamido) hexamethylenediamine | $C_{14}H_{26}N_4O_6S_2$ | 119-2 | 40.56 | 40.40 | 7.29 | 7.31 | 13.52 | 13.46 |
| <u>N,N'</u> -bis(<u>n</u> -morpholinesulfamido) piperazine | $C_{12}H_{24}N_4O_6S_2$ | 255-6 | 37.49 | 37.70 | 6.29 | 6.28 | 14.58 | 14.76 |
| <u>N,N'</u> -bis(dimethylsulfamido) hexamethylenediamine | $C_{10}H_{22}N_4O_4S_2$ | 120-1 | 36.34 | 36.28 | 7.93 | 7.94 | 16.95 | 17.04 |

Table X (cont.)

| <u>Compound</u> | <u>Empirical Formula</u> | <u>M.P. (°C.)</u> | <u>Carbon %</u> | | <u>Hydrogen %</u> | | <u>Nitrogen %</u> | |
|--|------------------------------|-----------------------|-----------------|--------------|-------------------|--------------|-------------------|--------------|
| | | | <u>Calcd.</u> | <u>Found</u> | <u>Calcd.</u> | <u>Found</u> | <u>Calcd.</u> | <u>Found</u> |
| <u>N,N'</u> -bis(dimethylsulfamido) piperazine | $C_8H_{20}N_4O_4S_2$ | 217-8 | 32.00 | 31.99 | 6.71 | 6.64 | 18.66 | 18.55 |
| <u>N,N'</u> -tris(<u>n</u> -cyclopenta- diethylenetriamine | $C_{19}H_{40}N_3O_6S_3$ | 129-3 | 41.89 | 41.78 | 7.40 | 7.51 | 15.43 | 15.73 |

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1. Dimethylsulfamyl chloride. - Dimethylamine hydrochloride (81.55 g., 1 mole) and sulfuryl chloride (268 g., 2 moles) were mixed together in a flask fitted with a reflux condenser. Gentle refluxing was continued for 12 hours, after which time the evolution of hydrogen chloride ceased. The mixture was cooled to 0°C. and treated carefully with a water solution of sodium carbonate to decompose the unreacted sulfuryl chloride. The product was then extracted with ether and the ether solution washed several times with water and dried over calcium chloride. After the removal of the ether, an oily material was obtained, which was purified by means of fractional distillation. The pure compound is a colorless oil which boils at 42°C./0.6 mm.

Anal. Calcd. for $C_2H_6ClNO_2S$: C, 16.74; H, 4.21; N, 9.76.

Found: C, 16.76; H, 4.20; N, 9.76.

2. N-morpholinesulfamyl chloride. - To a solution of 70 g. of sulfuryl chloride (0.5 mole) in 150 ml. of toluene, cooled in an ice-salt bath, there were added drop-wise with vigorous agitation 87.12 g. of morpholine (1.0 mole) at such a rate that the temperature of the reaction mixture was maintained below 0°C. Then water was added, and the mixture was allowed to warm to room temperature. The toluene layer was separated from the aqueous layer and was washed successively with water, with 10% hydrochloric acid, with sodium bicarbonate solution, and finally again with water. The solution was then dried over calcium chloride. The excess of toluene was first removed by distillation, and the residue was purified under reduced pressure, yielding a colorless oil, b.p. 76°C./0.3 mm.

Anal. Calcd. for $C_4H_8ClNO_2S$: C, 25.88; H, 4.34; N, 7.54.

Found : C, 25.99; H, 4.46; N, 7.50

3. N,N'-bis(diethylsulfamido)ethylenediamine. - Diethylsulfamyl chloride (17.1 g., 0.1 mole), dissolved in 70 ml. of ether, was placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. Ethylenediamine (6.0 g., 0.1 mole) was added drop-wise at room temperature with agitation. After the addition was completed, stirring was continued for 1 hour. The mixture was then treated with water and the ether layer separated and dried over calcium chloride. On distilling the excess of ether, a white compound was recovered, which was found to be insoluble in cold water but very soluble in most of the organic solvents. The pure compound, after recrystallization from alcohol, was a white, crystalline material, melting at 52°C. Yield 8.0 g. (49%).

Anal. Calcd. for $C_{10}H_{22}N_4O_4S_2$: C, 36.35; H, 7.93; N, 16.96.

Found : C, 36.36; H, 7.76; N, 16.73.

4. N,N'-bis(diethylsulfamido)hexamethylenediamine. - Diethylsulfamyl chloride (17.1 g., 0.1 mole) and hexamethylenediamine (12.0 g., 0.1 mole) dissolved in 100 ml. of benzene were placed in a flask equipped with a reflux condenser. Gentle refluxing was maintained for 3 hours. The hydrochloride was removed

by filtration and washed with benzene. The excess of solvent was then distilled off, leaving a yellow residue which was purified by several recrystallizations from carbon tetrachloride. The pure compound was a white, crystalline material, melting at 65°C. Yield 6.0 g. (31%).

Anal. Calcd. for $C_{14}H_{24}N_4O_4S_2$: C, 43.50; H, 8.86; N, 14.50

Found: C, 43.24; H, 8.52; N, 14.36

5. N,N'-bis(diethylsulfamido)piperazine. - Diethylsulfamyl chloride (17.1 g., 0.1 mole) and piperazine (19.42 g., 0.1 mole) dissolved in 100 ml. of alcohol were mixed together in a flask equipped with a reflux condenser. The reaction proceeds at room temperature while a white precipitate is formed. Gentle heating was maintained for 8 hours in order to complete the reaction. The hydrochloride was then separated by filtration and washed with alcohol. The alcoholic solution concentrated under vacuum. A yellowish residue was left. It was treated with water to remove traces of hydrochloride and filtered. The crude material after recrystallization from ether gave a white, crystalline compound which melted at 107-8°C. Yield 7.0 g. (39%).

Anal. Calcd. for $C_{12}H_{20}N_4O_4S_2$: C, 40.44; H, 7.92; N, 15.72

Found: C, 40.68; H, 7.73; N, 15.62.

6. N,N'-bis(n-cyclopentamethylenesulfamido)ethylenediamine. N-cyclopentamethylenesulfamyl chloride (9.175 g., 0.05 mole) was dissolved in 80 ml. of ether and placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. Ethylenediamine (3.0 g., 0.05 mole) was added drop-wise at room temperature with agitation. After the addition, stirring was continued for 2 hours. Upon adding water to the clear solution, a white precipitate insoluble in ether and water was formed. It was filtered, washed with water to remove traces of hydrochloride, and dried. The compound showed a great insolubility toward cold water, carbon tetrachloride, ether, and benzene. It was found to be very soluble in chloroform and alcohol. After recrystallization from alcohol it melted at 128-129°C. Yield 3.0 g. (34.0 %).

Anal. Calcd. for $C_{12}H_{22}N_4O_4S_2$: C, 40.67; H, 7.39; N, 15.81

Found: C, 40.82; H, 7.34; N, 15.51

7. N,N'-bis(n-cyclopentamethylenesulfamido)piperazine. - Piperazine (9.71 g., 0.05 mole) dissolved in 80 ml. of alcohol and cyclopentamethylene-sulfamyl chloride (9.175 g., 0.05 mole) were mixed together in a flask fitted with a reflux condenser. The reaction started at room temperature while a precipitate was formed. Gentle refluxing was then held for 2 hours. The precipitate was filtered and washed with alcohol, and the alcoholic solution concentrated under vacuum, leaving no residue. The mixture of compound and hydrochloride was then washed with cold water until the water solution did not give a positive test with silver nitrate. The dried product was found to be insoluble in cold water and in all the organic solvents but fortunately could be recovered from the mixture in high purity.

It is a white, crystalline material, which melts at 241-242°C. Yield 5.0 g. (48%)

Anal. Calcd. for $C_{14}H_{28}N_4O_4S_2$: C, 44.19; H, 7.42; N, 14.73

Found : C, 44.36; H, 7.26; N, 14.92.

8. N,N'-bis(n-cyclopentamethylenesulfamido)hexamethylenediamine. - Hexamethylenediamine (6.0 g., 0.05 mole) dissolved in 80 ml. of benzene and cyclopentamethylenesulfamyl chloride (9.175 g., 0.05 mole) were mixed together in a flask equipped with a reflux condenser. Gentle refluxing was maintained for 4 hours. The hydrochloride was removed by filtration and washed with benzene and the benzene layer concentrated under reduced pressure. A yellow residue was left, which was washed with water to remove traces of hydrochloride and filtered. The crude dried product, after several recrystallizations from carbon tetrachloride, yielded a white powder which melts at 105-106°C., sintering a few degrees before melting. Yield 5.0 g., (49%).

Anal. Calcd. for $C_{16}H_{34}N_4O_4S_2$: C, 46.81; H, 8.35; N, 13.65

Found : C, 46.70; H, 8.25; N, 13.48

9. N,N',N''-tris(n-cyclopentamethylenesulfamido)diethylenetriamine. - Diethylenetriamine (5.128 g., 0.05 mole) dissolved in 50 ml. of alcohol and n-cyclopentamethylenesulfamyl chloride (13.762 g., 0.075 mole) in 25 ml. of alcohol were mixed together in a flask fitted with a reflux condenser. The reaction started at room temperature and was exothermic. The mixture was left standing for 1 hour. Then gentle refluxing was maintained for 3 hours. The hydrochloride was separated by filtration and washed with alcohol, and the alcoholic layer was concentrated under vacuum, leaving a viscous oil. Upon adding water, the oily material was transformed into a sticky solid, which after recrystallization from alcohol gave in poor yield a white powder which melts at 129-130°C.

Anal. Calcd. for $C_{18}H_{40}N_6O_6S_3$: C, 41.89; H, 7.40; N, 15.43

Found: C, 41.78; H, 7.51; N, 15.73.

10. N,N'-bis(n-morpholinesulfamido)ethylenediamine. - N-morpholinesulfamyl chloride (9.128 g., 0.05 mole) was dissolved in 80 ml. of ether and placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. Ethylenediamine (3.0 g., 0.05 mole) was added drop-wise at room temperature with agitation. After the addition, stirring was prolonged for two hours. Upon adding water to the ether solution, a white precipitate insoluble in water and ether was formed. It was filtered, washed with water to remove traces of hydrochloride, and dried. The pure compound, after recrystallization from alcohol, was a crystalline material which melts at 130-131°C. Yield 3.0 g. (35%).

Anal. Calcd. for $C_{10}H_{22}N_4O_6S_2$: C, 33.51; H, 6.18; N, 15.63.

Found: C, 33.65; H, 6.06; N, 15.63.

11. N,N'-bis(n-morpholinesulfamido)hexamethylenediamine. - Hexamethylenediamine (6.0 g., 0.05 mole) dissolved in 80 ml. of benzene and n-morpholinesulfamyl chloride (9.28 g., 0.05 mole) were mixed together in a flask fitted with a reflux condenser. Gentle refluxing was maintained for two hours to complete the reaction. The precipitate which was formed was separated by filtration and washed with cold benzene. On concentrating the benzene layer, no residue was left. The solid material, insoluble in benzene, was then washed several times with water to remove the hydrochloride. The crude product, after recrystallization from alcohol, gave a white powder which melted at 119-120°C. Yield 5.0 g. (49%).

Anal. Calcd. for $C_{14}H_{30}N_4O_6S_2$: C, 40.56; H, 7.29; N, 13.52

Found : C, 40.40; H, 7.31; N, 13.46

12. N,N'-bis(n-morpholinesulfamido)piperazine. - Piperazine (9.71 g., 0.05 mole) dissolved in 80 ml. of alcohol and n-morpholine sulfamyl chloride (9.28 g., 0.05 mole) were mixed together in a flask equipped with a reflux condenser. The reaction took place at room temperature, and a white precipitate was formed. The mixture was then left standing for 2 hours. The compound, which was found to be insoluble in alcohol, was separated by filtration, and the residue was washed several times with water to remove the hydrochloride. The pure dried product was a white crystalline material which melted at 255-256°C. Yield 5.4 g. (56%).

Anal. Calcd. for $C_{12}H_{24}N_4O_6S_2$: C, 37.49; H, 6.29; N, 14.58.

Found: C, 37.70; H, 6.28; N, 14.76

13. N,N'-bis(dimethylsulfamido)hexamethylenediamine. - Hexamethylenediamine (12.0 g., 0.1 mole) dissolved in 100 ml. of benzene and dimethylsulfamyl chloride (14.35 g., 0.1 mole) were mixed together in a flask fitted with a reflux condenser. The reaction, which is exothermic, started at room temperature, and the mixture was left standing for 1 hour. Then gentle heating was continued for 2 hours in order to complete the reaction. The hydrochloride was removed by filtration and washed with benzene. The benzene layer was concentrated under reduced pressure leaving a dark residue. The crude material was washed with water, filtered, and dried. After recrystallization from alcohol, the pure product was a white crystalline material which melted at 120-121°C. Yield 10.0 g. (60%).

Anal. Calcd. for $C_{10}H_{20}N_4O_4S_2$: C, 36.34; H, 7.93; N, 16.95.

Found: C, 36.28; H, 7.94; N, 17.04.

14. N,N'-bis(dimethylsulfamido)piperazine. - Piperazine (19.4 g., 0.1 mole) dissolved in 100 ml. of alcohol and dimethylsulfamyl chloride (14.35 g., 0.1 mole) were mixed together in a flask fitted with a reflux condenser. The reaction is exothermic and proceeds at room temperature. The mixture was then left standing for 2 hours, after which time the precipitate was filtered and washed with alcohol. The compound, which is insoluble in alcohol, was separated from the hydrochloride by means of several treatments with cold water and dried. It was a white, crystalline material, which melted at 217-218°C. Yield 7.5 g. (50%).

Anal. Calcd. for $C_8H_{20}N_4O_4S_2$: C, 32.00; H, 6.71; N, 18.66

Found: C, 31.09; H, 6.64; N, 18.55.

E. Discussion

Dialkylsulfamyl chlorides, when reacted with polyamines, did not yield products the thermal stabilities of which were as promising as we hoped to achieve. Of the polyamines that have been used for synthesis purposes, piperazine produces sulfamide derivatives more stable thermally than those obtained when ethylenediamine, hexamethylenediamine, or diethylenetriamine are employed.

Although a great deal of effort has been expended thus far in order to increase the thermal stability of the sulfamide molecule, no promising results have been obtained. Perhaps the sulfur-nitrogen bond in the molecule of sulfamide is too weak to prevent the evolution of sulfur dioxide when sulfamide itself or its derivatives are heated above 200°C. All experimental evidence points to this conclusion.

VIII. Synthesis of Sodium Polysulfides and Their Reactions with Reactive Halogen Compounds

A. Introduction

In the past, the anhydrous alkali metal polysulfides have been prepared by direct combination of the elements, either with or without a solvent, or by reaction of sodium hydrosulfide with sulfur in ethanol solution (20). It has now been found that solutions of sodium hydrosulfide in anhydrous liquid ammonia will react with sulfur, thus providing another path to the synthesis of anhydrous sodium polysulfides (27). This reaction thus yields the di-, tetra-, penta-, and the questionable trisulfide of sodium.

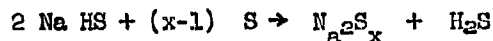
Reaction of solutions of sodium hydrosulfide and sulfur in liquid ammonia with reactive halogen compounds was further investigated as an extension of work already in progress.

B. Experimental

1. Synthesis of Sodium Polysulfides. - The general procedure consisted of condensing anhydrous ammonia onto a mixture of sodium hydrosulfide and sulfur. The distillation of the ammonia was done in a vacuum line. The anhydrous sodium hydrosulfide was synthesized by the reaction of sodium ethoxide with hydrogen sulfide in ethanol solution.

In a typical reaction for the preparation of sodium disulfide, 3.50 g. (0.0625 mole) of sodium hydrosulfide was mixed with 1.00 g. (0.0513 mole) of sulfur in an oven-dried reaction flask. The flask was then evacuated to a pressure of about 5 μ , flushed with dry nitrogen, and then evacuated again. This flask was cooled to -70°C. by a bath of Dry-Ice and methyl cellosolve. One hundred milliliters of ammonia was distilled then from sodium into the flask containing the mixture of hydrosulfide and sulfur. When the mixture of sodium hydrosulfide, sulfur, and ammonia was stirred (magnetically), dis solution occurred with the formation of a deep red color. Upon evaporation of the ammonia and heating the residue at 150°C and 5 μ pressure for 3 hours, pure sodium disulfide was obtained.

The reaction conforms to the following stoichiometry:



with the hydrogen sulfide actually being volatilized as ammonium hydrosulfide.

In a similar fashion one may obtain Na_2S_4 , Na_2S_5 , and a substance which gives an analysis consistent with the composition Na_2S_3 . Comparison of the x-ray diffraction patterns of Na_2S_2 and Na_2S_4 with that of Na_2S_3 indicates that the Na_2S_3 is a one to one mixture of Na_2S_2 and Na_2S_4 (26).

2. Reaction of Polysulfide Solutions with Halogen Compounds. - Methylene chloride will react with the red solutions of Na_2HS and sulfur in liquid ammonia to yield white to light yellow powders which are insoluble in all common solvents. The composition of these materials is variable and has been observed to range from $\text{CH}_2\text{S}_{1.5}$ to $\text{CH}_2\text{S}_{2.5}$. When warmed slightly, these white powders form rubbery green masses having a foul odor. Sharp x-ray diffraction patterns indicate that these substances are crystalline in nature.

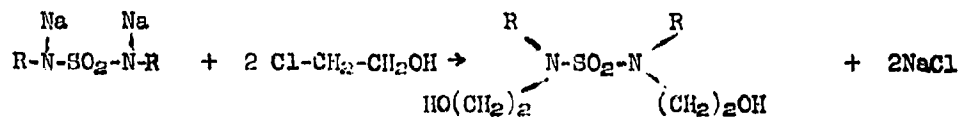
C. Discussion

The reaction of sodium hydrosulfide with sulfur in liquid ammonia provides a new convenient means for the preparation of anhydrous sodium polysulfides. The reactions of the hydrosulfide-sulfur solutions in ammonia with methylene chloride and similar compounds opens up an interesting area for investigation in the field of organic and inorganic polysulfides.

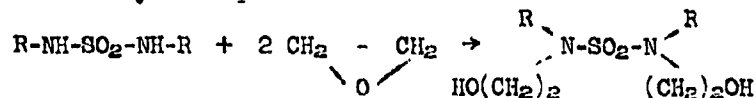
IX. Attempted Hydroxyalkylation of N-Substituted Sulfamides.

Sulfamide or its N-disubstituted derivatives are examples of typical classes of compounds susceptible to further alkylation on one or both nitrogen atoms. Displacement of the two remaining hydrogen atoms in the disubstituted derivatives of sulfamide by means of hydroxyethyl groups has been under investigation as a probable approach to the synthesis of N,N'-diethyl-N,N'-dihydroxyethylsulfamide derivatives. Among the several approaches that theoretically might lead to the synthesis of the desired products, the following may be mentioned.

(a) Reaction of the sodium salt of N-disubstituted sulfamides with ethylene chlorhydrine according to the following equation:

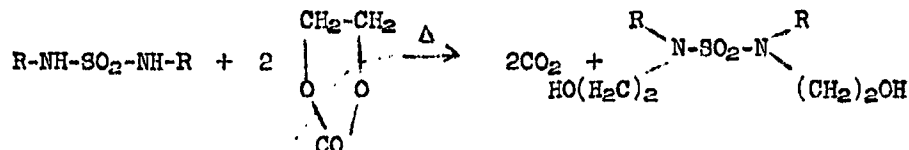


(b) Reaction of N-disubstituted sulfamides with ethylene oxide as indicated by the equation:



It has been our interest, however, to achieve the same results by using ethylene carbonate as principal reactant because of its known power as an alkylating agent in many organic reactions and to study the nature of these interesting direct nucleophilic substitutions. Furthermore, ethylene carbonate is a solid, and the reaction does not require an autoclave as in the case with ethylene oxide.

The reaction should proceed according to the following stoichiometry:



For this purpose the dialkylsulfamide and ethylene carbonate in a molar ratio 1:2 have been mixed together in the absence of solvent and heated for 10 hours at 150°C. At that temperature the reaction starts with evolution of carbon dioxide. Unfortunately, no definite product has been obtained as yet.

The very viscous material which was left did not solidify on standing, nor could it be recrystallized when dissolved in organic solvents. An attempt at purification by means of distillation under reduced pressure resulted in a violent decomposition. Although several experiments have been carried out and the results achieved not as promising as was expected, additional work will be carried out in the near future to elucidate this reaction more nearly completely.

X. Attempted Polycondensation Reactions of Sulfuryl Chloride and Polyamines

A. Introduction

Generally polycondensation, e.g., polyamidation and polyesterification, has been carried out in the past by means of melt polymerization. The procedure works properly but has some limitations. Temperatures, for example, average around or above 200°C. in order to permit removal of the low-molecular-weight products, and very often a difficult laboratory procedure is required.

It has been found more recently that the Schotten-Baumann reaction of an acid chloride with a compound containing an active hydrogen atom can be made the basis of a simple laboratory process, called interfacial polycondensation. Polycondensations carried out in this way are more rapid and can be effected in common equipment under ordinary experimental conditions.

In spite of the fact that the Schotten-Baumann reaction, which is run in an aqueous system, might lead to the partial hydrolysis of the acid chloride groups and inhibit the chain growth of the desired polymers, many polyurethanes, polyamides, polyureas, and even polysulfonamides have been prepared by this method (28) in excellent yields and high molecular weights.

Among the various organic and inorganic diacid chlorides used for the preparation of polysulfonamides, no mention was made to sulfuryl chloride as a starting material. We found it interesting, therefore, to attempt some polycondensation reactions by means the two-liquid-phase process in as much as the amine-acid chloride procedure in an organic solvent containing an acid acceptor is very difficult to control and yields hydrochloride as by product.

Theoretically, the reaction of sulfuryl chloride with a primary diamine should proceed according to the following stoichiometry:



An equimolar quantity of sodium hydroxide or sodium carbonate is used in the aqueous phase as acceptor of the hydrogen chloride produced. Besides purity, concentration of the reactants and correct pH control of the system are strongly recommended for the completion of the reaction.

Unfortunately, the several experiments thus far performed in which ethylenediamine, 1,6-hexanediamine, and piperazine were used have given no positive results. When redistilled sulfuryl chloride dissolved in methylene chloride was slowly added to a well-stirred aqueous solution of the polyamine containing sodium hydroxide or sodium carbonate, no polycondensation took place, but slow hydrolysis of the diacid chloride occurred. A solid was left on evaporating the organic layer, which excludes the possibility of formation of a soluble polymer. Chloroform and carbon tetrachloride have been used instead of methylene chloride and the molar concentration of the reactants varied, but in no instance could improvements be achieved. At the present, we must conclude that sulfuryl chloride seems not to be a suitable substance for the interfacial polycondensation procedure. The fact that under the same conditions other disulfonyl chlorides were found successful for the preparation of high molecular weight products lies perhaps in their lesser sensitivity in respect to hydrolysis. As a matter of fact the best polymers were obtained when aromatic disulfonyl chlorides were allowed to react with aliphatic polyamines (29). Sulfuryl chloride is too soluble in water to limit its tendency to hydrolysis even at low temperatures.

Although the results at the present time are not at all promising other experiments will be carried out in the future with special attention to the pH of the system in order to study further this kind of polycondensation.

XI. Deamination Products between Sulfamide and Polyamines

A. Introduction

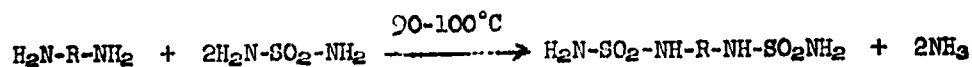
Since no inorganic-organic polymers could be obtained by means of the interfacial polycondensation procedure, another approach to the synthesis of the desired materials has been attempted. Sulfamide, with two amino groups in its structure and because of the increased acidity of its two nitrogen atoms due to the presence of the sulfone group, appears to be an ideal material for deamination reactions with polyamines. As a result of application of such a process, polymeric materials similar to those which could not be prepared by the Schotten-Baumann method might be obtained.

The capability of sulfamide to react with amines containing at least one replaceable hydrogen atom to give, with evolution of ammonia, N-substituted derivatives is well known. Very few compounds of this type are reported in the literature, however, due perhaps to the difficulty in obtaining the starting material. Condensation reactions of sulfamide with formaldehyde are also reported to give a variety of products, the course of the reaction being related to the pH of the solution. In mildly acidic (pH=4) or basic (pH=8) solutions, resins of quite low melting points were obtained (30). Later work (31) reported that under neutral conditions sulfamide and formaldehyde yield a cyclic compound, pentamethylenetetraminosulfone, m.p.=224-225°C. Finally, when this condensation was effected in strongly acidic solutions (32), tetramethylenedisulfotetramine, m.p.=225-260°C. (decompn.), was obtained.

Among primary diamines, sulfamide is reported to react with ethylenediamine and formaldehyde(3) to yield homopentamethylenetetraminosulfone, but no reactions of sulfamide and polyamines alone have been described. It has been our object during this period to repeat some experiments and to carry out new reactions in order to elucidate the behaviour of these condensation reactions of sulfamide.

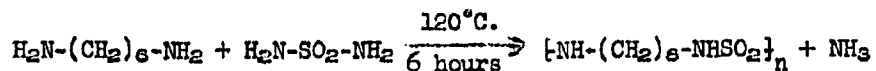
For this purpose, sulfamide was prepared by ammonolysis of sulfuric chloride in liquid ammonia according to the procedure of Goehring and coworkers(33). Surprisingly, when sulfamide and formaldehyde were allowed to react in the presence of ammonium hydroxide, e.g., under alkaline conditions, the compound was not pentamethylenetetraminosulfone as claimed by Paquin, but rather the tetramethylenedisulfotetramine, which Hecht and Henecka reported to have obtained in strongly acidic conditions (32). On the other hand, sulfamide and ethylenediamine in the presence of formaldehyde undergo condensation to yield homopentamethylenetetraminosulfone as reported earlier by Paquin (31). On the basis of this result, 1,6-hexanediamine, piperazine, and p-phenylenediamine were tested also with the object in view that new cyclic or linear condensation products might be formed. These latter diamines, however, behave in a different manner inasmuch as no cyclization or linear condensation takes place, and the polyamine methylol derivative is the final product. If sulfamide is allowed to react with diamines in the absence of the solvent, then deammonation readily occurs with the production of N-substituted sulfamides.

Experiments were run with sulfamide in the molar ratios 1:1 and 2:1 with respect to 1,6-hexanediamine, ethylenediamine, and piperazine. The general reaction proceeds as follows:



Piperazine and ethylenediamine when permitted to react at 90-100°C. in admixture with sulfamide, either in the molar ratio 1:1 or 1:2, led in any case to compounds according to the equation written above. No further deammonation could be obtained with the addition of sodium hydroxide as catalyst. The addition of sodium hydroxide, however, must be very small since imidodisulfamide might be produced (34).

Hexamethylenediamine behaves in a different manner toward sulfamide. The reaction is related to the concentration of the reactants, the temperature, and the time. In the molar ratio 1:2, 1,6-hexanddiamine and sulfamide undergo deammonation at 80-100°C. to yield the corresponding N,N'-disubstituted sulfamide derivative. However, in the molar ratio 1:1 at 120°C for 6 hours, further deammonation takes place with the production of a probably linear polymer as shown in the following equation:



The compound is a white powder, melting at 236-238°C. with decompn. It is insoluble in the gamut of organic solvents and in boiling water, but is fairly soluble in boiling DMF and DMSO. The not very sharp x-ray patterns and the high insolubility lead us to believe that the compound is polymeric in nature and corresponds to the structure shown above. Besides the strong absorption in the 3280 cm^{-1} region of its infra-red spectrum, which is characteristic of the -NH-stretching vibration, excludes any possibility of cross-linking.

B. Physical Properties

The N-substituted sulfamides here synthesized are all white crystalline materials, insoluble in most of the organic solvents, but slightly soluble in hot ethanol and boiling water. Consequently, these two solvents were found the best for purification.

C. Experimental

1. Sulfamide. - A 2-liter, 3-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a vent, was cooled at -70°C. by means of a Dry Ice-methylcellosolve bath. Some 300 ml. of liquid ammonia was then condensed into the flask at -70°C. A solution, consisting of 70 ml. of sulfonyl chloride in 500 ml. of petroleum ether (b.p. 90-110°C.) was added dropwise and with vigorous stirring over a period of 3 hours. The flask was then allowed to warm over night to room temperature to remove unreacted ammonia. The ether layer was removed by vacuum distillation and the product dried at room temperature. Two extractions, each with 250 ml. of ethyl acetate, were carried out. From each, white crystals resulted upon removal of the solvent. The remaining solid was dissolved in a solution obtained by diluting 20 ml. of 12 N hydrochloric acid to 150 ml. with water. This solution was evaporated and the brown solid obtained extracted with ethyl acetate. The combined crystals from the ethyl acetate extractions were dissolved in boiling ethanol. Cooling gave white, crystalline sulfamide with m.p. =92-93°C.

2. Tetramethylenedisulfotetramine. - Four and eight-tenths grams (0.05 mole) of sulfamide, 5 g. of a 37% solution of formaldehyde, and 30 ml. of ammonium hydroxide were mixed in a 250-ml. round flask equipped with a reflux condenser. On refluxing, a white solid began to separate. After 12 hours, the mixture was cooled over night to room temperature. The white precipitate was filtered, washed with cold water, and dried. It was

found to be insoluble in most of the organic solvents and slightly soluble in boiling water, from which it could be recrystallized as a white powder with m.p. =255-260° (decompn.).

Anal. Calcd. for $C_4H_8N_4S_2O_4$: C, 23.33; H, 3.33; N, 23.33

Found : C, 24.20; H, 3.79; N, 23.62

3. Homopentamethylenetetraminosulfone. - Four and eight-tenths grams (0.05 mole) of sulfamide, 3.9 g. (0.05 mole) of ethylenediamine hydrate, and 50 ml. of H_2O were placed in a 250-ml. round flask fitted with a reflux condenser. To that mixture, 20 g. of a 37% solution of formaldehyde was added rapidly. A white precipitate, due to the ethylenediamine-methylol derivative, was formed immediately. The temperature was then held at 80°C. for 4 hours, after which time the mixture was cooled at 0-5°C. The insoluble material was filtered, washed several times with cold water, and dried. It was found to be insoluble in several organic solvents and only slightly soluble in hot ethanol and hot water. After purification by recrystallization from water, the compound was a white, crystalline material with m.p. =205-206°C. (decompn.). Yield: 8.5 g. (82.5% of the theoretical).

Anal. Calcd. for $C_6H_{12}N_4SO_2$: C, 35.29; H, 5.92; N, 27.44

Found : C, 35.40; H, 5.91; N, 26.70

4. N,N'-bis(sulfamido)ethylenediamine. - Four and eight-tenths grams (0.05 mole) of sulfamide and 1.5 g. (0.025 mole) of ethylenediamine were mixed together without solvent in a 100-ml. round flask fitted with a reflux condenser. Upon heating at 90°C., ammonia was evolved. The flask was kept at that room temperature for 1 hour, after which time the mixture was cooled at room temperature. A solid material formed. It was insoluble in organic solvents but very soluble in cold and hot water. The purification was very difficult. However, the pure compound could be obtained by recrystallization from methanol. It was a white, crystalline material, which melted at 148-150°C.

Anal. Calcd. for $C_2H_{10}N_4S_2O_4$: C, 11.00; H=4.6; N=25.50

Found: C, 11.09; H=5.3; N=22.03

5. N,N'-bis(sulfamido)piperazine. - Four and eight-tenths grams (0.05 mole) of sulfamide and 4.85 g. (0.025 mole) of piperazine hexahydrate were mixed together without solvent in a 100-ml. round flask equipped with a reflux condenser. The temperature was held at 90-110°C. for 3 hours by gentle heating. After the evolution of ammonia ceased, the mixture was cooled at room temperature leaving a white solid material. This was filtered, washed several times with water, and finally purified by recrystallization from boiling water. The pure compound was a white, crystalline material, which melted at 241-243°C. (decompn.). Yield, 3.0 g. (49.50% of the theoretical).

Anal. Calcd. for $C_4H_{12}N_4S_2O_4$; C, 19.67; H, 4.95; N, 22.95.

Found : C, 19.69; H, 4.99; N, 22.68

6. N,N'-bis(sulfamido)hexamethylenediamine. - Two and nine-tenths grams (0.025 mole) of 1,6-hexanediamine and 4.8 g. (0.05 mole) of sulfamide were mixed together without solvent in a 100-ml. flask fitted with a condenser. After 2 hours of gentle heating at 90-100°C., the evolution of ammonia ceased. The solid which was formed was cooled at room temperature, treated with cold water, and filtered. It was insoluble in most of the organic solvents and slightly soluble in hot water and boiling ethanol. The pure compound, after recrystallization from ethanol, melted at 149-152°C. Yield, 3.0 g. (50% of the theoretical).

Anal. Calcd. for $C_6H_{18}N_4S_2O_4$: C, 26.27; H, 6.61; N, 20.43.

Found: C, 26.90; H, 6.49; N, 20.05.

7. Poly(hexamethylenesulfonamide). - Four and eight-tenths grams (0.05 mole) of sulfamide and 5.8 g. (0.05 mole) of 1,6-hexanediamine were mixed together in the absence of solvent in a flask fitted with a reflux condenser. The temperature was held at 120°C. for 6 hours. The tough solid, which was formed, was ground in a mortar and reduced to a white, fine powder. It was washed several times with cold water to stop polymerization and then with an aqueous solution of hydrochloric acid, after which it was dried. The crude material was then extracted in a Soxhlet apparatus for 48 hours with water, but no solid was recovered upon concentration of the solvent. The residue was found to be insoluble in the gamut of organic solvents and in boiling water and only fairly soluble in boiling DMF and DMSO. After recrystallization from DMF, the compound was a white powder which melted at 236-238°C. (decompn.).

Anal. Calcd. for $C_6H_{14}N_2SO_2$: C, 40.43; H, 7.92; N, 15.72.

Found: C, 39.85; H, 8.12; N, 16.46.

D. Discussion

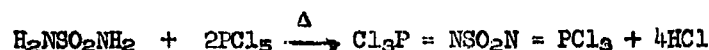
Reactions of sulfuryl chloride upon polyamines, as an attempt to effect interfacial polycondensation, have been shown to yield the hydrolysis of the acid chloride rather than the formation of linear polymers. The use of sulfamide instead of sulfuryl chloride leads to a variety of deamination products, among which a linear polymer could be isolated. The latter procedure seems promising for further investigation.

XII. Reactions of Sulfamide and of N,N-Dialkylsulfamides with Phosphorus(V) Chloride

A. Introduction

Among the various reactions that the aquo-ammonio and the ammonio sulfuric acid derivatives undergo, that with phosphorus(V) chloride is of particular interest. Kirsanov (35,36) has shown recently that both sulfamic acid and sulfamide, when caused to react with phosphorus(V) chloride give, respectively and in excellent yields, trichlorophosphazosulfonyl chloride and bis-trichlorophosphazosulfone as main products, provided the reactions are carried out with highly purified starting materials.

When sulfamide is employed, the stoichiometry of the reaction is given by:

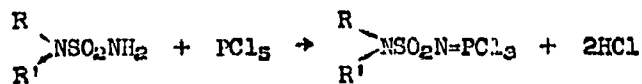


Not only does sulfamide behave in this fashion with respect to phosphorus pentachloride, but also its N,N-dialkyl derivatives gives the same general reaction. In fact, Kirsanov(37) was able to synthesize some dialkylamides of trichlorophosphazosulfuric acid by allowing the corresponding dialkylsulfamide to react with phosphorus pentachloride in the presence of carbon tetrachloride as a solvent. Inasmuch as the work thus far performed in this area is little and the total information available very sketchy, it has been of interest during this period to investigate in detail methods of synthesis and both chemical and physical properties for a number of such compounds.

All the dialkylsulfamides necessary for our purposes were obtained by ammonolysis of the corresponding sulfamyl chlorides. The dipropyl, the dibutyl, and the morpholino derivatives are described here for the first time.

As far as reactions of N,N-dialkylsulfamides with phosphorus(V) chloride are concerned, they can be effected by gently refluxing the two reactants in a 1:1 mole ratio in carbon tetrachloride as a solvent. All reactions are very exothermic, and some may occur even at room temperature depending on the solubility of the dialkyl sulfamide in the solvent. Thus, with morpholine and dimethylsulfamide, it was necessary to heat on the steam-bath in order to start the reaction, whereas diethyl-, dipropyl-, and dibutylsulfamide, being fairly soluble, reacted immediately at room temperature as soon as the reactants were mixed together. The yields of the corresponding N,N-dialkyl-trichlorophosphazosulfones are very good (ca. 90%), provided the starting materials are pure and all the operations involving weighing and handling phosphorus (V) chloride are performed in a dry-box.

The general reaction of an N,N-dialkylsulfamide with phosphorus(V) chloride proceeds as follows:



where: R=R', may be CH₃, C₂H₅, C₃H₇, C₄H₉, and C₄H₉O (from morpholine)

The following compounds were prepared by this type of reaction:

- I. Bis-trichlorophosphazosulfone
- II. N,N-dimethyl-trichlorophosphazosulfone
- III. N,N-diethyl-trichlorophosphazosulfone
- IV. N,N-dipropyl-trichlorophosphazosulfone
- V. N,N-dibutyl-trichlorophosphazosulfone
- VI. N-morpholine-trichlorophosphazosulfone

Numerical and analytical data for the compounds prepared are summarized in Table XI.

B. Chemical and Physical Properties

Bis-trichlorophosphazosulfone and the dialkylamides of trichlorophosphazosulfuric acid here synthesized are either high-boiling liquids or low-melting solids. All are very soluble in most of the organic solvents, and those which are solids may be purified by recrystallization from carbon tetrachloride. They react vigorously with water, alcohol, amines, and organo-metallic compounds. Special care must be taken in their handling because of hygroscopicity.

C. Experimental

1. N,N-Dipropylsulfamyl Chloride - A 500-ml., 3-necked flask, equipped with a mechanical stirrer, a dropping funnel and a reflux condenser, was cooled to -10°C . by means of an ice-salt bath. Sulfuryl chloride (134 g., 1.0 mole) was placed into the flask at -10°C . and propylamine (50.59 g., 0.5 mole) was added dropwise and with vigorous agitation over a period of 3 hours. After the addition was completed, the flask was warmed and the mixture poured into a 500-ml. one-necked flask fitted with a reflux condenser. Gentle refluxing was continued for 24 hours. The unreacted sulfuryl chloride was then slowly decomposed by pouring the mixture into an aqueous solution of sodium carbonate. The oil which separated was extracted with ether. After removal of the excess of ether, the pure compound was finally purified by distillation under reduced pressure. It is a colorless oil, b.p. $77^{\circ}/1.5\text{ mm}$. $n_D^{25}=1.4560$. Yield: 60 g. (60% of the theoretical).

Anal. Calcd. for $\text{C}_6\text{H}_{14}\text{NO}_2\text{SCl}$: C, 36.10; H, 7.07; N, 7.01.

Found: C, 36.22; H, 7.02; N, 6.85.

2. N,N-Dibutylsulfamyl Chloride. Sulfuryl chloride (134 g., 1.0 mole) was placed in a 500 ml., 3-necked flask, fitted with a mechanical stirrer, a dropping funnel and a reflux condenser. At -10°C ., 64.63 g. (0.5 mole) of dibutylamine was added dropwise to the sulfuryl chloride with vigorous agitation over a period of 3 hours. The flask was then warmed and the mixture transferred into a one-necked flask equipped with a reflux condenser. The mixture was then gently refluxed for 24 hours. The unreacted sulfuryl chloride was decomposed by treatment with an aqueous solution of sodium carbonate, and the resulting oily material extracted with ether. The ether layer was dried over calcium chloride and the solvent removed under vacuum. The pure compound was then obtained by distillation under reduced pressure. It is a colorless oil. b.p. $93^{\circ}/1\text{ mm}$. $n_D^{26} = 1.4590$. Yield: 55 g. (50% of the theoretical).

Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{NO}_2\text{SCl}$: C, 42.19; H, 7.96; N, 6.15

Found: C, 42.22; H, 7.82; N, 6.43

3. N,N-Dimethylsulfamide. - Some 200 ml. of liquid ammonia was condensed at -70°C . into a 500-ml., 3-necked flask, equipped with a mechanical stirrer, a dropping funnel and a vent. Dimethylsulfamyl chloride (35.87 g., 0.25 mole) was added in small portions with vigorous agitation, and stirring was continued for 6 hours after the addition was completed. The flask was then

Table XI
Properties and Analyses of the Dialkylamides of Trichlorophosphazosulfuric Acid

| Compound | Empirical Formula | M.P. (°C.) | B.P. (°C./mm.) | $n_D^{25^\circ\text{C.}}$ | Carbon Calcd. Found | Hydrogen Calcd. Found | Nitrogen Calcd. Found |
|---|--|------------|----------------|---------------------------|---------------------|-----------------------|-----------------------|
| bis-trichlorophosphazosulfone | $\text{N}_2\text{O}_2\text{P}_2\text{SCl}_6$ | 41-2 | - | - | - | - | 7.64 7.80 |
| <u>N,N</u> -dimethyl-trichloro phosphazosulfone | $\text{C}_2\text{H}_5\text{N}_2\text{C}_2\text{PSCl}_3$ | 74 | - | - | 9.26 9.75 | 2.33 2.73 | 10.80 10.72 |
| <u>N,N</u> -diethyl-trichloro phosphazosulfone | $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2\text{PSCl}_3$ | - | 113/0.25 | 1.5080 | 16.71 16.63 | 3.50 3.41 | 9.74 9.91 |
| <u>N,N</u> -dipropyl-trichloro phosphazosulfone | $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2\text{PSCl}_3$ | - | 113/0.005 | 1.5010 | 22.83 22.99 | 4.47 4.41 | 8.87 8.97 |
| <u>N,N</u> -dibutyl-trichloro phosphazosulfone | $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2\text{PSCl}_3$ | - | 140/0.05 | 1.4952 | 27.96 27.75 | 5.26 5.33 | 8.15 8.31 |
| <u>N</u> -morpholine-trichloro phosphazosulfone | $\text{C}_4\text{H}_8\text{N}_2\text{C}_3\text{PSCl}_3$ | 94 | - | - | 15.94 16.14 | 2.67 2.76 | 9.29 9.38 |

allowed to stand over night at room temperature to remove unreacted ammonia. The separation of the compound from ammonium chloride could be accomplished only upon prolonged extraction with benzene in a Soxhlet apparatus. On cooling the benzene solution, the pure compound was obtained as a white, crystalline material. M.P. 98°C. Yield: 20 g. (65% of the theoretical).

Anal. Calcd. for $C_2H_8N_2O_2S$: C, 19.36; H, 6.49; N, 22.58

Found: C, 19.38; H, 6.47; N, 22.63

4. N-Morpholinesulfamide - A 500-ml., 3-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a vent, was cooled at -70°C. by means of a Dry Ice-methylcellosolve bath. Some 250 ml. of liquid ammonia was then condensed into the flask. Morpholinesulfamyl chloride (46.40 g., 0.25 mole) was added in small portions, after which stirring was continued for 6 hours. The flask was then allowed to stand overnight at room temperature in order to remove the excess of ammonia. The crude material was treated with water to dissolve the ammonium chloride and the residue purified by recrystallization from ethanol. The pure compound was a white, crystalline material, m.p. 160-2°C. Yield: 25 g. (55% of the theoretical).

Anal. Calcd. for $C_4H_{10}N_2O_3S$: C, 28.92; H, 6.06; N, 16.86

Found : C, 29.05; H, 5.80; N, 17.06.

5. N,N-Dipropylsulfamide. Some 250 ml. of liquid ammonia was condensed at -70°C. into a 500-ml. 3-necked flask, fitted with a mechanical stirrer, a dropping funnel, and a vent. Dipropylsulfamyl chloride (60 g., 0.3 mole) was added in small portions with vigorous agitation, and stirring was continued for 6 hours after the addition was completed. The excess of liquid ammonia was allowed to evaporate by keeping the flask at room temperature. Inasmuch as after the removal of the ammonia part of the chloride was still unreacted, an additional 200 ml. of liquid ammonia was condensed into the flask and the procedure repeated. The compound was then separated from ammonium chloride by extraction with ether. Upon evaporation of the ether solution, a white solid was obtained, which was finally purified by recrystallization from n-heptane. The pure compound was a white, crystalline material, m.p. 69°C. Yield: 44 g. (85% of the theoretical).

Anal. Calcd. for $C_6H_{16}N_2O_2S$: C, 39.99; H, 8.95; N, 15.55

Found: C, 40.10; H, 8.95; N, 15.50

6. N,N-Dibutylsulfamide. A 500-ml., 3-necked flask, equipped with a mechanical stirrer, a dropping funnel and a vent, was cooled at -70°C., and 250 ml. of liquid ammonia were condensed into it. Dibutylsulfamyl chloride (52 g., 0.25 mole) was then added in small portions with vigorous agitation. After 56 hours of stirring, the flask was allowed to stand at room temperature in order to remove unreacted ammonia. At this point, another 200 ml. of liquid ammonia was condensed into the flask, and the entire procedure was repeated. The residue was extracted with boiling ether and the excess of ether removed under vacuum. The solid obtained was finally purified by recrystallization from n-heptane. The pure compound melted at 70°C. Yield: 35 g. (87.5% of the theoretical).

Anal. Calcd. for $C_8H_{20}N_2O_2S$: C, 46.15; H, 9.68; N, 13.46

Found: C, 45.91; H, 9.83; N, 13.71

7. Bis-trichlorophosphazosulfone. Fourteen grams (0.145 mole) of dry sulfamide and 60.68 g. (0.291 mole) of phosphorus(V) chloride were placed in a 250-ml. one-necked flask, equipped with a reflux condenser and a phosphorus(V) oxide drying tube. By means of an oil bath, gentle heating at 50-60°C. was maintained for 12 hours, during which time hydrogen chloride was evolved rapidly. The temperature was then raised to 100°C. and held there for another 5 hours. The viscous liquid obtained was heated at 130°C. under vacuum to remove traces of unreacted phosphorus(V) chloride. The oil was dissolved in 20 ml. of anhydrous ether, and on cooling at 0°C., a white solid precipitated. Because of the hygroscopic nature of the compound, filtration had to be performed in a dry-box. The pure compound is a white, crystalline material which melts at 41-42°C.

Yield: 50 g. (95% of the theoretical).

Anal. Calcd. for $N_2O_2P_2S_2Cl_6$: N, 7.64

Found: N, 7.80

8. N,N-Dimethyl-trichlorophosphazosulfone. Twenty grams (0.161 mole) of N,N-dimethylsulfamide, 33.57 g. (0.161 mole) of phosphorus(V) chloride, and 100 ml. of carbon tetrachloride were placed in a 250-ml., one-necked flask fitted with a reflux condenser and a drying tube. Upon gentle refluxing, hydrogen chloride was evolved rapidly, and in 3 hours a clear, white solution was obtained. Cooling at 0°C. gave a white precipitate. This was filtered and dried. The pure compound is a white, crystalline solid, which melts at 74°C.

Yield: 39 g. (93% of the theoretical).

Anal. Calcd. for $C_2H_6N_2O_2PSCl_3$: C, 9.26; H, 2.33; N, 10.80

Found: C, 9.75; H, 2.73; N, 10.72

9. N,N-Diethyl-trichlorophosphazosulfone. Thirty-four and forty-six hundredths grams (0.226 mole) of N,N-diethylsulfamide, 47.16 g. (0.226 mole) of phosphorus(V) chloride, and 150 ml. of carbon tetrachloride were placed in a 250-ml., one-necked flask fitted with a reflux condenser and a drying tube. On heating the mixture with a steam-bath, hydrogen chloride was evolved rapidly. After 2 hours, gas evolution ceased, and a clear solution was obtained. The excess of solvent was removed under vacuum, leaving a viscous oily material. The oil was finally purified by distilled under reduced pressure. The pure compound is a colorless oil, which boils at 113°C/0.25 mm. $n_D^{25} = 1.5080$ Yield: 55 g. (86% of the theoretical).

Anal. Calcd. for $C_4H_{10}N_2O_2PSCl_3$: C, 16.71; H, 3.50; N, 9.74

Found: C, 16.63; H, 3.41; N, 9.91

10. N,N-Dipropyl-trichlorophosphazosulfone. Thirty-four and two-tenths grams (0.189 mole) of N,N-dipropylsulfamide, 39.53 g. (0.189 mole) of phosphorus(V) chloride, and 100 ml. of carbon tetrachloride were placed in a 500-ml. round-bottomed flask equipped with a reflux condenser and a drying tube. The reaction takes place at room temperature with evolution of hydrogen chloride. The gentle heating on the steam-bath was continued for 3 hours, after which time the evolution of gas ceased. The excess of carbon tetrachloride was removed under vacuum, and the oily material which was left was purified by distillation under reduced pressure. The pure compound is a colorless oil, which boils at 113°C./0.005 mm. $n_D^{25} = 1.5010$ Yield: 50 g.

(83.5% of the theoretical).

Anal. Calcd. for $C_8H_{14}N_2O_2PSCl_3$: C, 22.83; H, 4.47; N, 8.87

Found : C, 22.99; H, 4.41; N, 8.97

11. N,N-Dibutyl-trichlorophosphazosulfone. Thirty grams (0.144 mole) of N,N-dibutylsulfamide, 30 g. (0.144 mole) of phosphorus(V) chloride, and 100 ml. of carbon tetrachloride were placed in a 500-ml., round-bottomed flask fitted with a reflux condenser and a drying tube. The reaction was very exothermic and started at room temperature. Then gentle refluxing on the steam-bath was continued for 3 hours, after which time the reaction was completed. The excess of carbon tetrachloride was removed under vacuum, leaving a viscous oily material. The pure compound, obtained by vacuum distillation, was a yellow oil which boils at $140^\circ C./0.05$ mm. $n_D^{25} = 1.4952$ Yield: 39.5 g. (80% of the theoretical).

Anal. Calcd. for $C_8H_{18}N_2O_2PSCl_3$: C, 27.96; H, 5.28; N, 8.15

Found : C, 27.75; H, 5.33; N, 8.31

12. N-Morpholine-trichlorophosphazosulfone. Eight and three-tenths grams (0.05 mole) of N-morpholinesulfamide, 10.41 g. (0.05 mole) of phosphorus(V) chloride, and 50 ml. of carbon tetrachloride were placed in a 250-ml., round-bottomed flask fitted with a reflux condenser and a drying tube. Gentle heating on the steam-bath was continued for 3 hours, after which time the evolution of hydrogen chloride ceased, and a clear solution was obtained. Upon cooling at $0^\circ C.$, a white precipitate was formed; it was filtered and dried. The pure compound is a white, crystalline material, which melts at $94^\circ C.$ Yield: 14 g. (93% of the theoretical).

Anal. Calcd. for $C_4H_8N_2O_3PSCl_3$: C, 15.94; H, 2.67; N, 9.29

Found : C, 16.14; H, 2.76; N, 9.38

D. Discussion

The reaction of sulfamide with phosphorus(V) chloride has been shown to be a general one. When it was applied to its N,N-disubstituted derivatives, the corresponding dialkylamides of trichlorophosphazosulfuric acid were obtained in excellent yields. This new family of compounds, containing the phosphazo group, opens another interesting field in research upon which our efforts will be concentrated in the near future.

XIII. Reactions of Bis-trichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric Acid with Grignard Reagents.

A. Introduction

The synthesis of bis-trichlorophosphazosulfone and of some dialkylamides of trichlorophosphazosulfuric acid as products of the interaction between sulfamide and its N,N-disubstituted derivatives with phosphorus(V) chloride, has been described. We also mentioned on that occasion that very few solvolytic

processes had been effected with those starting materials. It has been our object, therefore, to study the behaviour of these chlorides towards metal-organic compounds and in particular toward Grignard reagents.

Since alkyl and aryl chlorides react rather sluggishly with magnesium turnings in ether to form the alkyl or aryl magnesium chloride, the corresponding bromides were employed as being the most satisfactory for this purpose. A small crystal of iodine, however, must be added in order to start the reaction. In the first part of our investigation, phenylmagnesium bromide and *p*-tolylmagnesium bromide have been caused to react with bis-trichlorophosphazosulfone, *N,N*-dimethyltrichlorophosphazosulfone, and *N,N*-diethyltrichlorophosphazosulfone. The *N,N*-dipropyl, *N,N*-dibutyl, and morpholino derivatives were employed as well.

In every instance, complete replacement of the chlorine atoms by an aryl group takes place rather easily when at room temperature an ether or benzene solution of the chloride is dropped into an ether solution of a freshly prepared Grignard reagent, followed by gentle refluxing for the completion of the reaction.

Although no appreciable difficulty has been experienced in effecting the complete replacement of the chlorine atoms with phenyl and *p*-tolyl groups, the yields of corresponding *p*-tolyl derivatives were found to be slightly lower. The difference is perhaps due to the greater solubility of the *p*-tolyl compounds in several organic solvents and consequent increase in difficulty of crystallization, but other important factors could be involved as well.

Thus in order to obtain further information on these nucleophilic substitutions, reactions of the mentioned chlorides with *m*-tolyl-magnesium bromide and with the ortho-Grignard compound have been under study. As we suspected, when *m*-tolylmagnesium bromide is employed the nucleophilic attack on the phosphorus atom becomes more difficult, and it is practically non-existent in yielding completely substituted derivatives with the ortho-Grignard compound. Even with excess of Grignard reagent and upon prolonged refluxing of the reaction mixture, the yields of the compounds obtained from *m*-tolyl-magnesium bromide were found to be very low, and no complete substituted derivative could be isolated when *o*-tolylmagnesium bromide was employed.

We attribute the failure to steric effects which may play an important role in the inhibition of these condensation reactions. Another factor of possible importance is the tendency of the chlorides of pentavalent phosphorus acids to form insoluble complexes with the magnesium halide when treated with Grignard reagents. This tendency is of course increased by steric hindrance. A typical example is shown in the reaction of phosphorus(V) oxytrichloride with organo-magnesium compounds, which yields a mixture of phosphine oxide derivatives together with derivatives of phosphinic acid. The yield of the latter is increased by the use of branched alkyl or aryl groups (38,39).

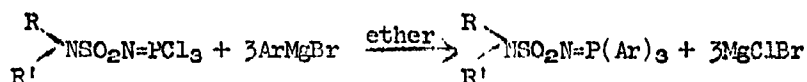
This complex-forming ability of the intermediates has been encountered in the course of our experiments. After the reaction was completed, product could not be found upon evaporation of the solvent. Furthermore, extraction of the gummy residue with different solvents did not give positive results. The desired compounds could only be separated upon decomposition of the complex with acidic solutions.

This suggests the possibility that with hindered Grignard reagents, the intermediates react with the magnesium halide to give an ether-insoluble complex which then, under heterogeneous conditions, is no longer capable of reacting with the organo-magnesium compound to yield complete substitution. Upon acidic hydrolysis, however, the complex can be broken, and phosphinic acid derivatives of the type $R_2NSO_2NP(OH)Ar_2$ or $R_2NSO_2NHP(O)Ar_2$ can be obtained.

This assumption is also substantiated by the fact that such compounds are soluble in aqueous sodium hydroxide solutions and can be reprecipitated upon acidification at pH ca. 6. The tri-substituted derivatives, by contrast, do not hydrolyze even in boiling aqueous sodium hydroxide.

All the reactions were carried out by slowly adding the chloride to an ether solution of excess Grignard reagent and refluxing for a period of 24 hours after addition was completed. The products were obtained upon hydrolysis of the complex with dilute hydrochloric acid or saturated ammonium chloride. Final purification can be achieved by recrystallization of the crude material from absolute ethanol or dilute ethanol.

The general reaction is illustrated by the following equation:



Where: $R = R'$, may be CH_3 , C_2H_5 , C_3H_7 , C_4H_9 and C_3H_5O (from morpholine) and $p\text{-CH}_3C_6H_4$, $m\text{-CH}_3C_6H_4$ and $o\text{-CH}_3C_6H_4$.

In the case in which bis-trichlorophosphazosulfone is employed, the stoichiometry is as follows:



Where: $Ar = C_6H_5$ and $p\text{-CH}_3C_6H_4$.

The following compounds were prepared by this type of reaction:

- I. Bis-triphenylphosphazosulfone
- II. N,N-dimethyl-triphenylphosphazosulfone
- III. N,N-diethyl-triphenylphosphazosulfone
- IV. N,N-dipropyl-triphenylphosphazosulfone
- V. N,N-dibutyl-triphenylphosphazosulfone
- VI. N,N-morpholine-triphenylphosphazosulfone
- VII. Bis-tri-*p*-tolylphosphazosulfone
- VIII. N,N-dimethyl-tri-*p*-tolylphosphazosulfone
- IX. N,N-diethyl-tri-*p*-tolylphosphazosulfone
- X. N,N-dipropyl-tri-*p*-tolylphosphazosulfone
- XI. N,N-dibutyl-tri-*p*-tolylphosphazosulfone
- XII. N,N-morpholine-tri-*p*-tolylphosphazosulfone
- XIII. N,N-dimethyl-tri-*m*-tolylphosphazosulfone
- XIV. N,N-diethyl-tri-*m*-tolylphosphazosulfone
- XV. N,N-morpholine-tri-*m*-tolylphosphazosulfone

B. Physical Properties

All the compounds here synthesized are white, crystalline, non-hygroscopic materials with reasonably high melting points. They are insoluble in cold and boiling water; insoluble in ether, petroleum ether, and *n*-heptane; fairly soluble in hot ethanol, carbon tetrachloride, and benzene; soluble in acetone and chloroform. Their purification is best effected by several recrystallizations from ethanol.

The infra-red spectra of chloroform solution and KBr pellets show an intense absorption in the 1140-1145 cm^{-1} region, which is associated with the symmetrical S-O vibration in the $-\text{SO}_2-$ grouping. The asymmetrical vibration, which usually occurs in the 1320-1340 cm^{-1} region disappears, while a new strong absorption band in the 1270-1300 cm^{-1} is constantly present. We attribute this vibration rather than to the pure $-\text{N}=\text{P}-$ stretch due to the $[-\text{S}-\text{N}=\text{P}-]$ group. The reason for this assumption lies in the

fact that in all our spectra the peaks in the 1300 cm^{-1} region are not well resolved and present a shoulder. This would indicate that there might be a coupling between the $-\text{SO}_2-$ asymmetric stretch and the pure $-\text{N}=\text{P}-$ vibration, thus giving rise to the strong vibration in the 1300 cm^{-1} region.

C. Thermal Stability and Liquid Range

The thermal stabilities of the compounds synthesized during this period have been evaluated according to the method described previously. Thermal stability measurements were carried out by heating in an inert atmosphere for 10 hours at 200°C. 0.2-0.5 g. of the sample and determining the loss of weight after that period. The compounds which gave a loss of weight less than 0.3 per cent at that temperature, under-went further heating at 250°C., for the same length of time, and their loss of weight was redetermined. Experimental data, in terms of uncorrected temperatures and of increasing weight loss, are given in Table I.

Inasmuch as in our early studies on *N*-substituted sulfamides, promising results in respect to thermal stability could not be achieved, we have attempted the synthesis of a new category of compounds in which the nitrogen atoms of sulfamide and of its *N*-substituted derivatives are linked to phosphorus atoms and the study of their behavior towards heat. Furthermore, typical aryl radicals such as phenyl and *p*-tolyl groups, have been placed on the phosphorus atoms by reaction with Grignard reagents.

Data from Table XII show clearly that at least at 200°C. almost all the compounds can be considered as stable thermally since the loss of weight is less than or of the order of 0.3 percent. Raising the temperature, however, gives remarkably increasing weight losses, which means that substantial thermal decomposition takes place rapidly at 250°C.

D. Experimental

1. Phenylmagnesium Bromide - Magnesium turnings (3.648 g. 0.15 mole), previously treated with a small crystal of iodine, were placed in a well-dried, 500-ml., 3-necked flask, fitted with a reflux condenser with a drying tube on top and a dropping funnel. Some 70 ml. of dry ether were quickly

Table XII
Properties of Bis-triarylphosphazosulfones and N,N-dialkyl-triarylphosphazosulfones

| Compound | Weight loss after 10 hrs. at 200°C. (g) | Weight loss after 10 hrs. at 250°C. (g) | M.p., °C. |
|--|--|--|--------------|
| Bis-tri-p-tolylphosphazosulfone | 0 | 3.2 | 226 |
| Bis-triphenylphosphazosulfone | 0 | 12.1 | 240-244 |
| N,N-dimethyl-triphenylphosphazosulfone | 0.13 | 8.0 | 156-158 |
| N,N-morpholine-triphenylphosphazosulfone | 0.16 | 8.4 | 181-182 |
| N,N-dipropyl-triphenylphosphazosulfone | 0.18 | 1.8 | 178-179.5 |
| N,N-dimethyl-tri-p-tolylphosphazosulfone | 0.25 | 1.63 | 196 |
| N,N-dibutyl-triphenylphosphazosulfone | 0.31 | - | 149 |
| N,N-dipropyl-tri-p-tolylphosphazosulfone | 0.40 | - | 175 |
| N,N-morpholine-tri-p-tolylphosphazosulfone | 1.20 | - | 129 |
| N,N-diethyl-triphenylphosphazosulfone | 2.40 | - | 127 |
| N,N-dibutyl-tri-p-tolylphosphazosulfone | 2.50 | - | 155 |

poured into the flask. While the mixture was stirred magnetically, bromobenzene (23.553 g., 0.15 mole) in 150 ml. of ether was added dropwise to the magnesium. After a short period of induction, the reaction starts immediately and continues until all the magnesium is dissolved.

2. Bis-triphenylphosphazosulfone - Eighteen and thirty-three hundredths grams (0.05 mole) of bis-trichlorophosphazosulfone in 50 ml. of ether, were slowly added to an ether solution of phenylmagnesium bromide (54.39 g., 0.3 mole) at room temperature over a period of 2 hours. After the addition was completed, gentle refluxing was continued for an additional 3 hours. The mixture was then cooled and slowly poured into a flask containing crushed ice and 40 ml. of concentrated hydrochloric acid solution. A solid, insoluble in water, separated immediately. It was filtered, washed several times with water, and dried. The pure compound was finally obtained by extracting with benzene in a Soxhlet apparatus for a period of 24 hours. It melted at 240-244°C. Yield: 10 g. (32.4% of the theoretical).

Anal. Calcd. for $C_{36}H_{30}N_2O_2SP_2$: C, 70.12; H, 4.90; N, 4.54.

Found: C, 70.54; H, 4.98; N, 4.70.

3. N,N-morpholine-triphenylphosphazosulfone - Fifteen grams (0.05 mole) of N,N-morpholinetrichlorophosphazosulfone in 200 ml. of benzene, were added in small portions to an ether solution of phenyl magnesium bromide (27.201 g., 0.15 mole) at room temperature over a period of 1 hour. The mixture was allowed to stand for 3 hours, after which time the excess of benzene was driven off under vacuum. The residue was dissolved in boiling ethanol, from which upon cooling, a white precipitate was formed. It was filtered and washed with water to dissolve the magnesium halide until the water solution gave a negative test with silver nitrate. The residue was purified by recrystallization from ethanol. The pure compound was a white crystalline material, which melts at 181-182°C. Yield: 3 g. (29% of the theoretical).

Anal. Calcd. for $C_{22}H_{23}N_2O_3SP$: C, 61.96; H, 5.43; N, 6.57.

Found: C, 61.72; H, 5.39; N, 6.39.

4. N,N-dipropyl-triphenylphosphazosulfone - Twenty grams (0.0563 mole) of N,N-dipropyltrichlorophosphazosulfone in 50 ml. of ether was slowly added to an ether solution of phenylmagnesium bromide (36.26 g., 0.2 mole) at room temperature over a period of 1 hour. After the addition was completed, gentle refluxing was continued for an additional 2 hours. The reaction mixture was then carefully poured into a flask containing crushed ice and 40 ml. of concentrated hydrochloric acid solution. The solid material which separated was extracted with 1000 ml. of benzene in a separatory funnel. The benzene layer was dried over $CaCl_2$, and the excess of solvent was driven off under vacuum, leaving a solid. The pure compound, after two recrystallization from ethanol, was a white, crystalline material, which melted at 178-179.5°C. Yield: 13.40 g. (48% of the theoretical).

Anal. Calcd. for $C_{24}H_{26}N_2O_2SP$: C, 65.43; H, 6.63; N, 6.36

Found: C, 65.10; H, 6.48; N, 6.58.

5. N,N-diethyl-triphenylphosphazosulfone. Fourteen and thirty-seven hundredths grams (0.05 mole) of N,N-diethyltrichlorophosphazosulfone in 50 ml. of ether, was slowly added to an ether solution of phenyl-magnesium bromide (27.19 g., 0.15 mole) at room temperature over a period of 2 hours. After the addition was completed, the mixture was gently refluxed for 12 hours. The reaction mixture was then slowly poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which was separated was extracted with benzene and the organic layer dried over calcium chloride. The excess of benzene was driven off under vacuum and the solid, which was obtained, purified by recrystallization from ethanol. The pure compound was a white, crystalline solid, melting at 127°C. Yield: 13.60 g. (66.0% of the theoretical).

Anal. Calcd. for $C_{22}H_{25}N_2O_2PS$: C, 64.07; H, 6.11; N, 6.79.

Found: C, 63.90; H, 6.17; N, 6.89.

6. N,N-dimethyl-triphenylphosphazosulfone. Twelve and ninety-seven hundredths grams (0.05 mole) of N,N-dimethyltrichlorophosphazosulfone in 150 ml. of benzene was slowly added, with stirring, to an ether solution of phenylmagnesium bromide (27.19 g., 0.15 mole) at room temperature. After the addition of the chloride, gentle refluxing was held for an additional 12 hours. The mixture was then decomposed by slowly pouring it into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which separated was extracted with benzene and the organic layer dried over calcium chloride the excess of benzene was distilled under reduced pressure and the solid which was left purified by recrystallization from ethanol. The pure compound was a white, crystalline material, which melted at 156-158°C. Yield: 7.0 g. (36.8% of theory).

Anal. Calcd. for $C_{20}H_{21}N_2O_2PS$: C, 62.49; H, 5.50; N, 7.28

Found: C, 62.52; H, 5.33; N, 7.18

7. N,N-dibutyl-triphenylphosphazosulfone. Eight and six-tenths grams (0.025 mole) of N,N-dibutyltrichlorophosphazosulfone in 50 ml. of ether was slowly added to an ether solution of phenylmagnesium bromide (13.59 g., 0.075 mole) at room temperature. After the addition was completed, the mixture was stirred and gently refluxed for 12 hours. The reaction mixture was then poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which was separated was extracted with benzene and the organic layer dried over calcium chloride. Upon distillation of the excess of benzene, a solid material was left. It was purified by recrystallization from ethanol, yielding the pure compound which melted at 149°C. Yield: 6.0 g (51.3% of the theoretical).

Anal. Calcd. for $C_{26}H_{33}N_2O_2PS$: C, 66.65; H, 7.10; N, 5.98

Found: C, 66.76; H, 7.10; N, 6.21

8. p-tolylmagnesium Bromide. Magnesium turnings (3.648 g., 0.15 mole), previously treated with a small crystal of iodine, were placed in a well-dried, 500-ml., 3-necked flask, equipped with a reflux condenser, with a drying

tube on top, and a dropping funnel. Some 70 ml. of dry ether was placed in the flask. While the mixture was stirred magnetically, p-bromotoluene (25.65 g., 0.15 mole) in 150 ml. of ether was added drop-wise to the magnesium. After a short heating to overcome the period of induction, the reaction starts and proceeds smoothly until all the magnesium is dissolved.

9. N,N-dibutyl-tri-p-tolylphosphazosulfone. Eight and six-tenths grams (0.025 mole) of N,N-dibutyltrichlorophosphazosulfone in 50 ml. of ether was added at small portions to a well-stirred solution of p-tolylmagnesium bromide (14.64 g., 0.075 mole) at room temperature. After the addition of the chloride, the mixture was stirred and refluxed for 12 hours. The reaction mixture was then decomposed by pouring it into a flask containing 200 g. of crushed ice and 50 ml. of 12 M hydrogen chloride. The solid which separated, was extracted with benzene and the organic layer dried over calcium chloride. After the removal of the excess of solvent, the solid material which was left was purified by recrystallization from ethanol. The pure compound was a white, crystalline solid, that melted at 155°C. Yield: 6.0 g. (48.0% of theory).

Anal. Calcd. for $C_{28}H_{39}N_2O_2PS$: C, 68.21; H, 7.70; N, 5.48

Found : C, 68.34; H, 7.59; N, 5.55

10. N,N-dimethyl-tri-p-tolylphosphazosulfone. Twelve and ninety-seven hundredths grams (0.05 mole) of N,N-dimethyltrichlorophosphazosulfone in 150 ml. of benzene was slowly added to an ether solution of p-tolylmagnesium bromide (29.29 g., 0.15 mole) at room temperature with stirring. After the addition was completed, the reaction mixture was gently refluxed for 12 hours. The mixture was then slowly poured into a flask containing 200 g. of crushed ice and 50 ml. of 12 M hydrochloric acid. The solid which separated was extracted with benzene and the benzene layer dried over calcium chloride. The excess of solvent was removed under reduced pressure, and the crude product which was left was purified by recrystallization from ethanol. The pure compound was a white, crystalline material which melted at 196°C. Yield: 6.45 g. (30.0% of the theoretical).

Anal. Calcd. for $C_{23}H_{27}N_2O_2PS$: C, 64.77; H, 6.38; N, 6.56

Found : C, 64.68; H, 6.43; N, 6.26

11. Bis-tri-p-tolylphosphazosulfone. Nine and sixteen-hundredths grams (0.025 mole) of bis-trichlorophosphazosulfone in 50 ml. of ether was slowly added to an ether solution of p-tolylmagnesium bromide (29.29 g., 0.15 mole) at room temperature over a period of 2 hours. After the addition was completed, gentle refluxing was continued for an additional 12 hours. The mixture was then cooled and slowly poured into a flask containing crushed ice and 50 ml. of 12 M poured into a flask containing crushed ice and 50 ml. of 12 M hydrochloric acid solution. A solid, insoluble in water, separated. It was extracted with benzene and the benzene layer dried over calcium chloride. After the removal of the solvent, the solid which was left was purified by several recrystallizations from

ethanol. The pure compound melted at 226°C. Yield: 5.0 g. (29.4% of theory).

Anal. Calcd. for $C_{42}H_{42}N_2O_2P_2S$: C, 72.02; H, 6.04; N, 4.00

Found : C, 71.79; H, 6.10; N, 3.94.

12. N,N-dipropyl-tri-p-tolylphosphazosulfone. Fifteen and seventy-eight hundredths grams (0.05 mole) of N,N-dipropyltrichlorophosphazosulfone in 50 ml. of ether were slowly added to an ether solution of p-tolylmagnesium bromide (29.29 g., 0.15 mole) at room temperature. The mixture was gently refluxed and stirred vigorously for 12 hours after the addition was completed. The crude compound was then obtained by pouring the reaction mixture into a flask containing 200 g. of crushed ice and 50 ml. of 12 M. hydrochloric acid. The solid which separated was extracted with benzene and the organic layer dried over calcium chloride. After the removal of the excess of benzene by distillation under vacuum, the solid was purified by recrystallization from ethanol. The pure compound was a white, crystalline material, melting at 175°C. Yield: 9.6 g. (40% of theory).

Anal. Calcd. for $C_{27}H_{25}N_2O_2P_2S$: C, 67.19; H, 7.31; N, 5.80

Found: C, 66.99; H, 7.30; N, 5.93

13. N,N-morpholine-tri-p-tolylphosphazosulfone. Seven and five-tenths grams (0.025 mole) of N,N-morpholinetrichlorophosphazosulfone in 80 ml. of benzene were added at small portions to an ether solution of p-tolylmagnesium bromide (14.66 g., 0.075 mole) at room temperature with stirring. The mixture was then gently refluxed for 12 hours after the addition was completed. The reaction product was poured into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M. hydrochloric acid, from which a solid separated. It was extracted with benzene and the organic layer dried over calcium chloride. The solid which was left after removal of the solvent was purified by recrystallization from ethanol, and the pure compound was a white, crystalline material melting at 129°C. Yield: 2.3 g. (20.0% of theory).

Anal. Calcd. for $C_{25}H_{29}N_2O_3PS$: C, 64.09; H, 6.24; N, 5.98

Found : C, 64.36; H, 6.26; N, 5.91

14. N,N-dimethyl-tri-m-tolylphosphazosulfone. Six and fourty-eight hundredths grams (0.025 mole) of N,N-dimethyltrichlorophosphazosulfone in 100 ml. of benzene was slowly added to an ether solution of m-tolylmagnesium bromide (19.53 g., 0.1 mole) at room temperature with stirring. After the addition was completed, the reaction mixture was gently refluxed for 24 hours. The excess of Grignard was decomposed by addition of 100 ml. of a saturated aqueous solution of ammonium chloride. The compound was then extracted with benzene. The organic layer was dried over calcium chloride and the excess of solvent removed by distillation under vacuum. The crude product which was left was finally purified by several recrystallizations from ethanol. The pure compound obtained in ca. 10% yield, was a white,

crystalline solid which melted at 158-9°C.

Anal. Calcd. for $C_{23}H_{27}N_2O_2PS$: C, 64.77; H, 6.38; N, 6.56

Found : C, 64.91; H, 6.45; N, 6.31

15. N,N-morpholine-tri-m-tolylphosphazosulfone. Seven and five-tenths grams (0.025 mole) of N,N-morpholinetrichlorophosphazosulfone in 100 ml. of benzene was added at small portions to an ether solution of m-tolylmagnesium bromide (19.53 g., 0.1 mole) at room temperature with stirring. The mixture was then refluxed for an additional 24 hrs. after the addition was completed. The reaction product was poured into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M hydrochloric acid. The product was extracted with benzene and the benzene layer dried over calcium chloride. The solid which was left after the removal of the solvent was washed with an aqueous solution of sodium hydroxide, dried, and finally purified by recrystallization from dilute ethanol. The pure compound was a white, crystalline material melting at 123-125°C. obtained in ca. 10% yield.

Anal. Calcd. for $C_{25}H_{29}N_2O_2PS$: C, 64.09; H, 6.24; N, 5.98

Found: C, 64.93; H, 6.44; N, 6.10

16. Attempted Preparation of N,N-morpholine-tri-p-tolylphosphazosulfone. Seven and five-tenths grams of N,N-morpholinetrichlorophosphazosulfone in 100 ml. of benzene was slowly added at room temperature to a well-stirred ether solution of p-tolylmagnesium bromide (19.53 g., 0.1 mole). Gentle refluxing was maintained for 24 hours after the addition was completed. The excess of Grignard reagent was decomposed by pouring the reaction mixture into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M hydrochloric acid. The solid which separated was extracted with benzene and the benzene layer dried over calcium chloride. After the removal of the excess of solvent, the crude product was purified by several recrystallizations from ethanol. The compound which was obtained, gave m.p. 173-174°C. and microanalysis agrees fairly good for the disubstituted phosphinic acid derivative.

Anal. Calcd. for $C_{18}H_{23}N_2O_4PS$: C, 54.81; H, 5.87; N, 7.10

Found: C, 56.32; H, 5.87; N, 7.45

E. Discussion

It has been shown during this investigation that both bis-trichlorophosphazosulfone and the dialkylamides of trichlorophosphazosulfuric acid, undergo complete arylation when caused to react with phenylmagnesium bromide with the production of a new class of compounds never described previously.

With p-tolylmagnesium bromide complete substitution is still possible although the final products are recovered in lower yields. Besides, the broad melting points of the crude materials and the fact that they can be obtained in high purity only after several recrystallizations from ethanol lead us to believe that partially substituted compounds are obtained as by-products.

When *m*- and *o*-tolylmagnesium bromides are employed, steric hindrance becomes most apparent. The yields of the *m*-compounds are quite low and those of the *o*-compounds practically non-existent.

XIV. Synthesis of Trichlorophosphazosulfonyl Chloride

A. Introduction

The reaction of sulfamic acid with phosphorus(V) chloride was first investigated by Ephraim and Gurewitsch (40), who hoped to secure the unknown sulfamyl chloride according to the following reaction:



Inasmuch as pure sulfamyl chloride was never isolated from the reaction mixture, the authors concluded that sulfamic acid reacted with two molecules of phosphorus pentachloride, the second molecule of phosphorus pentachloride decomposing into chlorine and phosphorus trichloride and the latter then combining with the sulfamyl chloride to form a stable binary compound of the formula $\text{ClSO}_2\text{NH}_2 \cdot \text{PCl}_3$. The reaction then had to proceed according to the following stoichiometry:



For many years it has been common belief that that was the final product which one can obtain. Recently, however, Kirsanov (41) proved that the product of the interaction between sulfamic acid and phosphorus pentachloride is actually altogether different. He noted that only hydrogen chloride and not chlorine is evolved in the course of the reaction and that the reaction product is not a dark-brown liquid which does not recrystallize as claimed by Ephraim and Gurewitsch, but rather a transparent liquid which quickly solidifies to a white crystalline mass after the removal of the phosphorus oxychloride. The final product proved to be a definite compound, i.e. trichlorophosphazosulfonyl chloride, which is formed according to the following equation:



Since trichlorophosphazosulfonyl chloride when slowly heated under vacuum undergoes an interesting decomposition to yield two isomers of sulfanuric chloride, it has been of interest during this synthesis period to prepare some of this material as a useful intermediate for our future synthesis of sulfanuric chloride. For this purpose, the Kirsanov procedure has been found reliable and to give the product in a 75.0% yield. The synthesis is achieved by allowing dried sulfamic acid to react with pulverized phosphorus(V) chloride in the mole ratio 1:2 either in the presence of a little carbon tetrachloride as a solvent or in the absence of solvent. For better results, however, it is advisable always to carry out the reaction with a slight excess of sulfamic acid.

Upon heating at 80°-90°C by means of an oil bath, the mixture liquefies readily with rapid evolution of hydrogen chloride and after 24 hours the reaction can be considered completed. After removal of the excess of unreacted sulfamic acid by filtration, the solvent and the phosphorus oxytrichloride are distilled off under reduced pressure. The remaining liquid

crystallizes quickly when chilled, giving a white solid mass saturated with liquid. The precipitate is filtered and pressed down in a dry-box. The melting point is 32-33°C.

B. Physical Properties

Trichlorophosphazosulfonyl chloride, like the parent bis-trichlorophosphazosulfone, is a very reactive and highly hygroscopic material. For this reason special precautions must be used in its handling. Filtration of the crude product must be performed in a dry-box, and the use of a sintered glass funnel is recommended. If a filter paper is used and some moisture is present, hydrolysis takes place readily with enough heat to cause the paper to burn. Consequently trichlorophosphazosulfonyl chloride must be handled with care in the presence of all substances containing hydroxy-groups.

Pure trichlorophosphazosulfonyl chloride is a white, crystalline material which shows a m.p. of 32-33°C. It is insoluble in water and fairly soluble in most of the organic solvents. It is usually obtained in reasonable purity directly from the reaction mixture so that purification is often not necessary. However, purification by recrystallization from petroleum ether (b.p. 110°C.) can be achieved, provided such operation is performed in a dry-box and the solvent has been previously treated with concentrated sulfuric acid in order to remove all the unsaturated hydrocarbons.

C. Experimental

1. Trichlorophosphazosulfonyl Chloride. Forty-eight and fifty-four hundredths grams (0.5 mole) of dry and pulverized sulfamic acid, 208.31 g. (1.0 mole) of phosphorus(V) chloride, and 50 ml. of carbon tetrachloride were placed in a 500-ml., one-necked flask equipped with a reflux condenser and a drying tube. All operations, including weighing of the reactants, were performed in a dry-box. By means of an oil bath, heating at 90-100°C, was maintained for ca. 24 hours, after which time the evolution of hydrogen chloride ceased. The volatile products were removed by vacuum distillation and the remaining clear, viscous oil cooled at 0°C. White crystals started to precipitate immediately. The precipitate was filtered and pressed out in a dry-box at 0°C. Upon chilling the filtrate, more crystalline material settled down. It was filtered and pressed out, and the two precipitates were combined. The pure trichlorophosphazosulfonyl chloride is a white, crystalline material, which melts at 33-35°C. However, should the material melt at 23-25°C., purification by recrystallization from petroleum ether (b.p. 90°C.) is recommended. Yield 178.0 (70% of theory).

Anal. Calcd. for NO_2PSCl_4 : N, 5.58

Found : N, 5.52

D. Attempted Preparation of Tribromophosphazosulfonyl Bromide

Although both trichlorophosphazosulfonyl chloride and sulfanuric chloride have been successfully synthesized, the corresponding bromo derivatives are at the present time unknown.

We have approached the synthesis of tribromophosphazosulfonyl bromide by allowing sulfamic acid to react with phosphorus(III) bromide and bromine, hoping that the reaction would follow the trend noted with sulfamic acid and phosphorus(V) chloride. Little success, however, has been achieved, since thus far in our experiments reaction seems not to occur, and unreacted sulfamic acid has been recovered in stoichiometrical quantity.

Experiments were run either in carbon tetrachloride or in *g*-tetrachloroethane as solvents. When sulfamic acid and phosphorus tribromide in the mole ratio 1:2 were allowed to react in the presence of carbon tetrachloride and an excess of bromine for two days at 90°C., unreacted sulfamic acid and phosphorus pentabromide were recovered upon sublimation, indicating that no interaction actually did occur. Neither was reaction noted using *g*-tetrachloroethane as a solvent and refluxing the reactants in the same mole ratios at 120°C. for one week. Upon distillation, bromine and phosphorus tribromide were obtained, the residue being constituted by unreacted sulfamic acid.

XV. Synthesis of Sulfanuric Chloride by Thermal Cleavage of Trichlorophosphazosulfonyl Chloride

A. Introduction

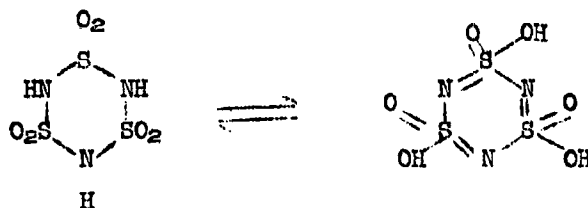
It is well known that in the ammonolysis of sulfuryl chloride either with gaseous or liquid ammonia, other deammonation products such as imidoammonium sulfamide and sulfimide are produced, in addition to sulfamide as a main product. Even though sulfimide, because of its instability could not be isolated as such, Traube (42) assumed he had secured the correspondent silver salt. The silver salt of sulfimide was also believed to have been obtained by Traube (42) from the products of the thermal decomposition of sulfamide.

It was only later (43) that it was shown that Traube's salts were actually salts of a trimer of sulfimide, e.g. salts of trisulfimide. All the attempts to isolate the hydrogen compound, however, have so far failed, thus suggesting that trisulfimide, like sulfimide, must be a very unstable compound. Recently, a tetrameric form of sulfimide as a silver salt, as well as a methyl derivative, have been obtained by Appel and Goehring (44) by allowing ammonia to react with excess sulfur trioxide in nitromethane solution.

All of this indicates that monomeric sulfimide, if it is formed, must be very unstable and must readily stabilize itself by forming six and eight-membered rings.

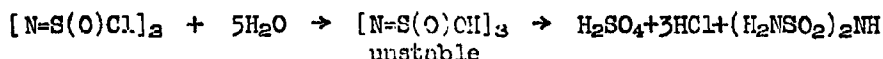
During our study on the sulfur-nitrogen system, it has been of interest to investigate a sulfur-nitrogen ring compound of relative stability, and sulfanuric chloride has been chosen because of its potential and interesting properties. Again it should be pointed out that, although sulfanuric chloride is readily accessible, the corresponding acid, i.e., sulfanuric acid, has not been isolated. This is neither surprising nor unexpected since we may regard sulfanuric acid as an isomer of trimeric sulfimide.

The two materials can in fact be considered to exist in the two tautomeric forms



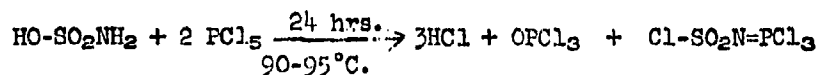
and the acid, like trisulfimide cannot be isolated as the hydrogen compound itself.

This is furtherly substantiated by the fact that hydrolysis of sulfanuric chloride leads to sulfanuric acid only as an unstable intermediate with imidodisulfamide, sulfuric acid, and hydrochloric acid being the final products (45).



Sulfanuric chloride on the other hand, is quite a stable material. The synthesis of this compound can be accomplished by any of the following procedures:

1. Reaction of sulfamic acid with phosphorus(V) chloride and thermal decomposition of the product (46,47).



2. Reaction of a mixture of sulfuryl chloride and thionyl chloride with gaseous ammonia (48). The sulfanuric chloride is obtained by sublimation of the reaction products under vacuum.

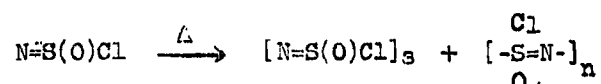
3. Oxidation of thiazyl chloride with sulfur trioxide (49).



Of the three procedures available, the thermal decomposition of trichlorophosphazosulfonyl chloride is the one which gives the most satisfactory synthesis of sulfanuric chloride. Furthermore, two isomers, the α and β -forms, can be obtained. Goehring's procedure, which involves the reaction of a mixture of sulfuryl chloride and thionyl chloride in the molar ratio 2:1 with gaseous ammonia at $-80^\circ C$., yields, among other deammonation products, only the α form of sulfanuric chloride and that in low yield. The method involving the oxidation of thiazyl chloride (trimer) with sulfur trioxide does not seem very practicable because of the difficulties which one would encounter in the preparation of the thiazyl chloride.

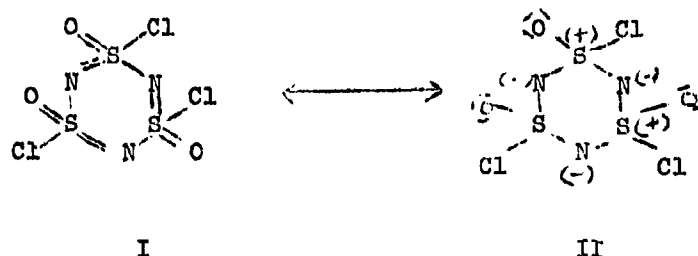
Trichlorophosphazosulfonyl chloride, on the other hand, can be readily prepared in 75.0% yield by the reaction of sulfamic acid with phosphorus(V) chloride. Upon heating the chloride at 130-140°C at a pressure of ca. 5 mm. for 3 hours while a stream of dry air is slowly passed through the substance, phosphorus oxytrichloride is released almost quantitatively, and the residue consists mainly of a mixture of isomers of sulfanuric chloride. Two substances (α and β) were isolated from the reaction product, and at least three more substances are believed to be present although they have not been isolated yet.

Inasmuch as the recovery of phosphorus oxytrichloride is almost quantitative and the yields of the two isomers are quite low (24.0% for the α form and 18.0% for the β) in comparison to the overall yield, it is reasonable to assume that monomeric sulfanuric chloride can undergo further transformations, polymerization, in particular.



Substances α and β contain no hydrogen or phosphorus, the formula being $\text{N}=\text{S}(\text{O})\text{Cl}$, and their molecular weight being equivalent to $[\text{N}=\text{S}(\text{O})\text{Cl}]_3$.

The materials appear to possess a ring structure with either alternating single and double bonds between nitrogen and sulfur atoms, or with alternating positive sulfur atoms and negative nitrogen atoms as:



One form melts at 144-145.5°C, and by analogy with cyanuric chloride it is called α -sulfanuric chloride. It may be called also 1,3,5-trichloroxo-1,3,5-trithiatiazine. The other form melts at 47°C. and is called β -sulfanuric chloride. Kirsanov suggested the two forms to be cis and trans isomers, the cis isomer with the three chlorine atoms on one side of the ring and the trans isomer with two chlorine atoms on one side of the ring and the third chlorine on the opposite side of the ring. Such an assumption, however, implies a planar ring. This has been shown recently not to be the case (50). X-ray studies on α -sulfanuric chloride have shown the crystals to be orthorhombic, with four molecules per unit cell of dimensions $a = 7.60 \text{ \AA}$, $b = 11.46 \text{ \AA}$, $c = 10.10 \text{ \AA}$. and bond lengths: $\text{S}-\text{N} = 1.58 \text{ \AA}$, $\text{S}-\text{Cl} = 2.00 \text{ \AA}$, and $\text{S}-\text{O} = 1.43 \text{ \AA}$. The arrangement of the bonds around the sulfur has been found to be roughly tetrahedral, and the $\text{S}-\text{N}-\text{S}$ angles to be 120°.

Thus formula(II) proposed as an alternative by Kirsanov, contributes insignificantly to the overall molecular structure. Furthermore since the sulfur-nitrogen bond distances are identical and quite close to the double-bond distance (1.56 Å), delocalization of the π -electrons must occur with alternating single and $p\pi-d\pi$ double bonds. The three chlorine atoms have been found to be all axial, and a chair configuration has been assigned.

No data are presently available as far as the structure of β -sulfanuric chloride is concerned. Inasmuch as it is an isomer of α -sulfanuric chloride, a chair configuration with three oxygen atoms axial and three chlorine atoms equatorial as well as the boat form might be assigned. More work on this area, therefore, has to be done before such an assignment can be established.

In the course of our investigation, several experiments to cleave the trichlorophosphazosulfonyl chloride have been performed under different conditions. In all instances, cleavage did occur only when the reaction mixture was heated at 130-140°C and when the pressure in the system was maintained at ca. 8-10 mm.

The separation of α and β isomers has been effected with a slight modification of Kirsanov procedure. After the thermal cleavage went to completion the product left in the distillation flask was extracted several times with hot *n*-heptane, from which upon cooling large crystals settled. The precipitate was filtered, and the excess of solvent was driven off under vacuum. The combined materials, which consist mainly of a mixture of α and β sulfanuric chloride, were sublimed then under high vacuum. The β -sulfanuric chloride sublimes readily at room temperature at 0.005 mm., whereas the α -sulfanuric chloride sublimes at 60-80°C. under the same pressure.

After extraction of the α and β isomers, the remaining viscous oily residue was found to be very hygroscopic and insoluble in several organic solvents.

B. Physical Properties

The α and β sulfanuric chlorides are white, crystalline, hygroscopic materials, which melt without decomposition at 144-146°C. and at 46-47.5°C. respectively. The β form hydrolyzed more readily than the α form and its melting point is depressed by the presence of moisture. Both can be stored, however, for a long period of time in a desiccator over sulfuric acid or phosphorus(V) oxide without appreciable change in their composition.

Both forms are insoluble in water, in which they hydrolyze slowly; readily soluble in organic solvents such as ether, benzene, ethyl acetate; sparingly soluble in carbon tetrachloride and chloroform; and very slightly soluble in *n*-heptane and petroleum ether. The last two solvents were found the best for their purification.

O. Experimental

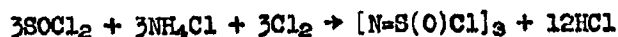
α and β Sulfanuric Chloride. Two hundred twelve grams (0.85 mole) of trichlorophosphazosulfonyl chloride (m.p. 33-35°C.) was placed in a distillation flask fitted with a deflagmetor and an inlet tube for dry air. The receiver was chilled at -70°C. by means of a freezing mixture. Dry air, previously desiccated with calcium chloride, was continuously passed through the substance in order to maintain the pressure in the system at c.a. 8-10 mm. Heating was held at 100°C., and the temperature was then slowly raised to 130°C. At this temperature, thermal decomposition started and phosphorus oxytrichloride began to distill rapidly. After 1 hour at 130°C., the temperature was raised to 140°C. for an additional one hour and finally to 150°C. for a short period of time. Usually, after 2.5 hours, the distillation of phosphorus oxytrichloride ceases, and the thermal cleavage can be considered finished. A total of 115 g. of phosphorus oxytrichloride were recovered in the chilled receiver, which means that 90.0% of the trichlorophosphazosulfonyl chloride underwent cleavage.

The dark residue in the distillation flask quickly solidified to a dark mass when the flask was kept at room temperature. The α and β sulfanuric chlorides were extracted from the reaction products by means of hot *n*-heptane. Upon cooling, large crystals separated, which were filtered and dried. The excess of solvent was removed *in vacuo*, and some more material was recovered. The solids were combined, and the separation of the two isomers was achieved either by sublimation under high vacuum or by fractional crystallization from *n*-heptane or petroleum ether b.p. 90°C. Sublimation works well since the α -sulfanuric chloride sublimes readily at 80°C. under high vacuum, whereas the β form sublimes at room temperature under the same vacuum. No difference in melting point was found between the material obtained by sublimation and that obtained by recrystallization from *n*-heptane. The α -sulfanuric chloride melts at 144-145°C., the β -form at 46-47°C.; both without decomposition. Yields: α -sulfanuric chloride, 12.0 g. (14.5% of theory); β -sulfanuric chloride 8.0 g. (9.8% of theory).

| | | | |
|--|----------|-------------|---------|
| <u>Anal.</u> Calcd. for α (NSOCl) | N, 14.36 | M.W. Calcd. | 292.578 |
| Found: | N, 14.47 | Found | 300 |
| Calcd. for β (NSOCl) | N, 14.36 | M.W. Calcd. | 292.578 |
| Found: | N, 14.21 | Found | 294 |

D. Attempted Preparation of Sulfanuric Chloride by Reaction of Thionyl Chloride with Ammonium Chloride in the Presence of Chlorine

We have found it interesting, in dealing with the preparation of sulfanuric chloride, to attempt the direct synthesis of this material by the reaction of thionyl chloride with ammonium chloride as a source of nitrogen, in the presence of chlorine as an oxidizing agent. Sym-tetrachloroethane was used as a solvent in our experiments. Reactions have been carried out under different conditions of time and temperature and always with a large excess of ammonium chloride. The reaction should proceed according to the following stoichiometry:

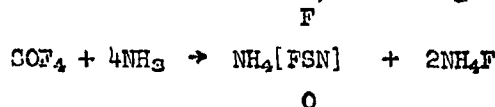


Unfortunately even after refluxing the reactants at 110-130°C. for one week, the reaction has failed to yield any product. Ammonium chloride was in all instances recovered unchanged thus indicating that the nitridation of thionyl chloride did not occur as expected. In fact, the reaction could start only if oxidation of sulfur(IV) to sulfur(VI) by the action of chlorine takes place. The absence of such an oxidation to produce even as an unstable intermediate the unknown thionyl tetrachloride may perhaps be the reason for failure of the reaction.

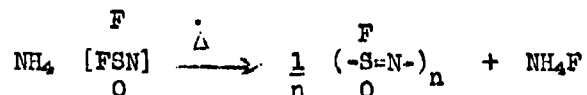
E. Attempted Preparation of Sulfanuric Fluoride by Metathetical Exchange of Sulfanuric Chloride

Inorganic aromatic systems such as the phosphonitrilic chlorides and thiazyl chloride have been successfully converted into the corresponding fluorine compounds either by the use of fluorinating agents like potassium fluorosulfinate, silver fluoride, and lead fluoride or by metathetical exchange with sodium fluoride in acetonitrile and nitrobenzene as solvents.

The synthesis of sulfanuric fluoride has not been reported as yet although the corresponding chloride can be successfully synthesized by several different procedures. The only reference in the literature(51) describes the synthesis of polymeric sulfanuric fluoride by the reaction of thionyltetrafluoride with ammonia, according to the following equation:



The ammonium salt upon sublimation there yielded a polymer as



There was no indication, however, whether the trimer was found among the decomposition products. It has been of interest, therefore, to attempt the synthesis of α and β sulfanuric fluoride by the metathesis of the corresponding chlorides with sodium fluoride in nitrobenzene as a solvent. Moreover, if such a synthesis could be attained successfully, the availability of α and β sulfanuric fluoride would permit a study of the fluorine nuclear magnetic resonance spectra and consequently a possible speculation as to the stereochemistry of the α and β forms.

Nitrobenzene was chosen as a solvent because of its high boiling point with the hope that the sulfanuric fluoride, if formed during the metathetical exchange, could be volatilized and subsequently trapped in relatively high purity in a vessel chilled at -70°C. Such a procedure which works excellently for the preparation of the phosphonitrilic fluorides, has failed, however, to yield the sulfanuric fluorides.

Reactions were carried out always in the presence of a large excess of sodium fluoride and at temperatures of 100°C., 130°C., and 180°C. In no case, even upon refluxing with stirring of the reaction mixture for 24 hours, could product be recovered in the chilled container. The nitrobenzene solution, slightly colored at low temperatures, became darker and darker upon refluxing, and after 24 hours it appeared to be completely black. Neither could product or unreacted starting sulfanuric chloride be recovered after distillation of the excess of solvent and extraction of the residue with several organic solvents.

This suggests that decomposition and not exchange may occur during the course of the reaction. These preliminary failures, though, do not allow us to conclude that exchange is impossible, but rather than that nitrobenzene may not be a suitable solvent. Our efforts in the future will be extended to the synthesis of this interesting material, using different and lower boiling solvents.

F. Discussion

Of the methods available for the preparation of sulfanuric chloride, Kirsanov's procedure has been shown to be the most suitable. Although yields are not very satisfactory, they are greater than those obtained by any other known procedure, and in addition two geometrical isomers are obtained. The thermal cleavage, however, requires a more complete investigation to permit identification of the reaction residue in which some other interesting decomposition products may still be contained. The metathetical exchange reaction of α -sulfanuric chloride with sodium fluoride in nitrobenzene has failed to produce the desired fluorine compound. No exchange was noticed during the course of the reaction but rather only the decomposition of the starting material.

XVI. Dipole Moment Measurements of α and β -Sulfanuric Chlorides

A. Introduction

The synthesis of α - and β -sulfanuric chloride by the thermal cleavage of trichlorophosphazosulfonyl chloride has been discussed previously. On the same occasion, we also pointed out, that during the cleavage the two forms were produced in yields ca. 24.0 and 18.0%, respectively. Other experiments carried out recently in this area have fully confirmed these results, and molecular-weight determinations by the vapor pressure method have shown that the molecular weights are of the same order for both materials. The products appear to differ only in melting point.

On the basis of such results, it is reasonable to assume that isomerism must be involved in the molecule of sulfanuric chloride although the cis and trans configurations are to be excluded on the basis of a recent x-ray study on the crystal of α -sulfanuric chloride. As a result of such investigation, the ring has been found not to be planar and the chair configuration has been assigned to the α - form of sulfanuric chloride.

The structure of β -sulfanuric chloride remains unknown. Inasmuch as the electric dipole moment is strictly related to the symmetry of a molecule, we have found it interesting to determine this constant as a possible approach to the identification of the β -isomer.

It is known that when a medium is placed between the plates of a capacitor, the capacitance is increased by a factor ϵ known as the dielectric constant. If C_0 is the capacitance with a vacuum and C the capacitance with the medium between the plates of the condenser, the dielectric constant ϵ is given by the following ratio:

$$\epsilon = \frac{C}{C_0}$$

Since the introduction of any medium increases the capacitance while the charge on the condenser plates must remain unchanged, the electric field between the plates must be reduced by the same factor ϵ . (52).

The reduction in the electric field may be due to two effects. In the first instance, which is always true whether the molecule of the medium has a permanent dipole moment or not, a separation of the positive and negative charges within each molecule tends to take place. The molecules are said to undergo a distortion polarization, P_D . If, however, the molecule of the medium has a permanent dipole moment, a second effect known as orientation polarization, P_O , will be present.

Both the molar distortion polarization and the molar orientation polarization have the dimensions of a volume, and it can be said that the total molar polarization, P_M , is given by the following equation:

$$P_M = P_O + P_D$$

Moreover the distortion polarization, P_D arises in two ways: First, the electrons in the molecules will be displaced with respect to the nuclei towards the positive pole of the applied field. This effect is known as the electron polarization, often called also molar refractivity, P_E . Second, the nuclei will be slightly displaced with respect to one another giving rise to the atom polarization, P_A . Thus we can say that:

$$P_D = P_E + P_A$$

and that the total molar polarization is given by:

$$P_M = P_O + P_E + P_A$$

Applying the Debye equation to the total molar polarization we have:

$$P_M = P_O + P_D = \frac{4\pi N_0}{3} \left(\alpha_D + \frac{\mu^2}{3kT} \right) \quad (I)$$

If we restrict our considerations to dilute solutions of polar molecules in non-polar solvents, we can express the total molar polarization also

by the Clausius-Mossotti equation:

$$\frac{P_M}{d} = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d} \quad (II)$$

Equating expressions (I) and (II) for the total molar polarization, we obtain:

$$\frac{(\epsilon - 1)}{\epsilon + 2} \frac{M}{d} = \frac{4\pi N_0}{3} \left(\frac{\alpha_D}{d} + \frac{e^2}{3KT} \right) = \frac{P_M}{d} \quad (III)$$

In order to derive μ from equation (III), two different procedures can be followed. By means of the temperature-method, it can be shown that under normal conditions of measurements, α_D and α_A are temperature independent. We can then measure the dielectric constant ϵ and the density d over a range of temperature and plot $\frac{P_M}{d}$, calculated from equation (I), against $1/T$. From equation (II), the slope of the graph will be equal to $4\pi N_0 e^2 / 9K$, and the intercept of the line at $1/T = 0$ will give the value of $\frac{\alpha_D}{d}$ (53). Although the evaluation of μ by the temperature method appears to be a simple process, there are actually several difficulties. It involves the assumption that μ is independent of temperature, and this is not always true. Moreover, not all substances are stable over a sufficiently wide range of temperature for this method to be applied.

Thus a second method, known as the refractivity-method, has therefore been recommended to eliminate the effect of distortion polarization. The refractivity method is based on the fact that the speed of response of the three types of polarization (electron, atom, and orientation) to an oscillatory electric field differs greatly. Furthermore, a simplification can be introduced through the Maxwell relationship that the dielectric constant is equal to the square of the refractive index, provided the refractive index is measured at a sufficiently high frequency for the orientation polarization to be absent. This latter method, though preferable to the temperature method, has some disadvantages also. We cannot allow for the solvent effect due to interactions between solutes and solvent molecules, and we have to allow for the atom polarization, P_A , even though there are no ways of evaluating it. Such a value, however, is usually very small and can be estimated to be between 5 and 15 per cent of P_E .

Such a procedure is the one we have used in the determination of the dipole moment of α and β sulfanuric chlorides. Among the several approaches available for the determination of P_M and P_E , we have applied the Halverstadt-Kumler equation. Such a procedure is an extension of the original Debye equation for the calculation of the total molar polarization:

$$P_M = P_{f1} + P_{f2} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_{f1}}{d} + \frac{M_{f2}}{d} + \dots$$

If P_M is calculated by using weight fractions (W_f) instead of molar fractions (f), a linear relationship still holds between dielectric constants

and specific volumes and weight fractions. The procedure is also much simpler since the molecular weight of the solvent need not be known. Disregarding the whole mathematical calculation, the Halverstadt-Kumer expression, which gives the specific total polarization, is as follows:

$$P_M = \frac{3\alpha v_0}{(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2} (v_0 + \beta)$$

where α and β represent respectively, the limiting values of $\partial\epsilon/\partial w_2$ and $\partial v/\partial w_2$ at zero concentration, v_0 the specific volume of the solvent, and ϵ_1 the dielectric constant of the solvent. The total molar polarization is then given by:

$$P_M = P_M \times M.W.$$

The specific electron polarization may be derived from the measured values of the refractive index, using the analogous relationship for the molar polarization:

$$P_E = \frac{3\delta v_0}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2} (v_0 + \beta)$$

where ϵ_1 is replaced by n_1^2 and δ is the limiting value of $\partial n^2/\partial w_2$ at zero concentration. The total molar refractivity will then be:

$$P_E = P_E \times M.W.$$

Having now the values of P_M and P_E , it is possible to evaluate P_0 and finally the dipole moment by using the following formula:

$$\begin{aligned} \mu &= 0.0128 \cdot 10^{-18} \text{ u.e.s.} \sqrt{P_0 \times T^\circ K} \\ &= 0.0128 \sqrt{P_0 \times T^\circ K} \text{ D.} \end{aligned}$$

For our purposes, the dielectric constants of pure benzene and of several benzene solutions of α - and β -sulfanuric chloride were determined by means of a capacitor at 25°C. The respective specific volumes were determined at the same temperature with a calibrated pycnometer, whereas the refractive indices of the colorless solutions were measured with a differential refractometer at the 436 m μ line of mercury (54). Values of 3.81 D and 2.19 D were obtained for α - and β -sulfanuric chloride respectively.

B. Experimental

α - and β -sulfanuric chlorides were recrystallized from *n*-heptane until sharp melting points of 144-145.5°C. and 47°C. were reached. Benzene was redistilled over phosphorus(V) oxide and stored over sodium wire for

24 hours. In the experiments performed, the following nomenclature has been used:

w_2 = weight fraction; ϵ_1 = dielectric constant of benzene; ϵ_{12} = dielectric constants of solutions; V_1 = specific volume of benzene; V_{12} = specific volumes of solutions; $\chi = \partial \epsilon_{12} / \partial w_2$; $\beta = \partial V_{12} / \partial w_2$; $\chi = \partial n^2_{12} / \partial w_2$; P_M = total molar polarization; P_E = molar refractivity; P_O = molar orientation polarization; and μ = dipole moment. All measurements were carried out at 25°C. (298°K.). The values of χ , β , and χ were obtained graphically.

Results are summarized in Tables XIII, XIV, and XV.

C. Discussion

The dipole moments of α - and β -sulfanuric chlorides in benzene have been determined and found to be of the order of 3.80 D and 2.19 D respectively. If we consider a bond moment as a vector quantity directed along the line of the internuclear axis, we may approximate the total dipole moment of a polyatomic molecule as given by the vector sum of the various bond moments.

Inasmuch as the chair configuration with all the chlorine axial, has been recently assigned to α -sulfanuric chloride, it is expected that this substance must possess the greatest dipole moment in respect to the other possible forms. β -sulfanuric chloride is undoubtedly less polar since its dipole moment has been found to be 2.19 D. Thus either another chair form or the boat configuration might be assigned to its molecule.

To which form it might belong, it is not possible to say on the basis of dipole moment speculations only. Further x-rays studies are necessary in order to define such an establishment.

XVII. References

1. M. K. Snyder: Doctoral Dissertation, University of Illinois, Urbana, Illinois (1956).
2. A. V. Kirsanov, Y. M. Zolotov, and N. L. Egorova: J. Gen. Chem. (U.S.S.R.), 20, 2339 (1950).
3. M. Goehring, J. Heinke, H. Malz, and G. Roos: Z. anorg. u. allgem. chem., 273, 200 (1953). See also M. Goehring and H. Hohenschutz: *ibid.*, 276, 47 (1954).
4. R. E. Eibeck: Report, Chemistry 404, University of Illinois, Urbana, Illinois (1958).
5. Behrend, R., Ann. Chem. 222, 125 (1884).
6. Wheeler, K. W. and Degering, F., J. Am. Chem. Soc., 66, 1242 (1944).
7. Frejacques, Jean L. M., U.S. Pat. 2, 498, 539 Feb. 21 (1950).
8. Denivelle, L., Bull. soc. chim. France [5] 3, 2143 (1936).
9. Binkley, W. W. and Degering, F., J. Am. Chem. Soc. 61, 3050 (1939).

Table XIII

Measurement of Electric Dipole Moment

| Weight fraction w_2 | Dielectric constant of solutions ϵ_{12} | Specific volume of solutions v_{12} | Square of refractive indices n^2_{12} |
|--------------------------|--|---|---|
| 0.01900 | 2.3770 | 1.114 | 2.2455 |
| 0.0100 | 2.3280 | 1.120 | 2.2440 |
| 0.00604 | 2.3060 | 1.123 | 2.2437 |

$$\epsilon_1 = 2.2724 \quad v_1 = 1.1260 \quad n^2_1 = 2.2440$$

$$\alpha = 5.50; \quad -\beta = 0.70; \quad \gamma = 0.093; \quad P_M = 336; \quad P_E = 41; \quad P_O = 295$$

$$\mu = 0.0128 \sqrt{P_O \times T^\circ K.} = 0.0128 \sqrt{295 \times 298}$$

$$= 0.0128 \sqrt{88,000} = 3.80 \text{ D.}$$

Table XIV

Measurement of Electric Dipole Moment

| Weight fraction w_2 | Dielectric constants of solutions ϵ_{12} | Specific volumes of solutions v_{12} | Square of Refractive indices n_{12}^2 |
|--------------------------|---|--|---|
| 0.02230 | 2.4000 | 1.1290 | 2.2518 |
| 0.01310 | 2.3470 | 1.1360 | 2.2506 |
| 0.00644 | 2.3110 | | 2.2500 |

$$\epsilon_1 = 2.2724$$

$$v_1 = 1.167$$

$$n_1^2 = 2.2440$$

$$\alpha = 5.50; -\beta = 0.70; \gamma = 0.093; P_M = 348; P_E = 52.6; P_O = 295.4$$

$$\mu = 0.0128 \sqrt{P_O \times T^\circ K.} = 0.0128 \sqrt{295.4 \times 298}$$

$$= 0.0128 \sqrt{88.000} = 3.80 \text{ D}$$

Table XV
Measurement of Electric Dipole Moment

Inasmuch as α , and β sulfanuric chlorides are isomers, the densities and the refractive indices of their solutions do not differ greatly within the experimental error. Consequently, for the calculation of the dipole moment of β -sulfanuric chloride only the variations of the dielectric constant have been determined. The molar refractivity has been calculated by using the values of β and χ obtained graphically in the determination of the dipole moment for α -sulfanuric chloride.

| Weight fraction w_2 | Dielectric constants of solutions ϵ_{12} |
|--------------------------|---|
| 0.009712 | 2.297 |
| 0.006174 | 2.290 |
| 0.003376 | 2.285 |

$$\epsilon_1 = 2.2724 \quad v_1 = 1.1446 \quad n_1^2 = 2.2440$$

$$\alpha = 1.88; -\beta = 0.70; \gamma = 0.093; P_M = 141.8; P_E = 43.3; P_0 = 98.5$$

$$\begin{aligned} \chi &= 0.0128 \sqrt{P_0 \times T^\circ K} = 0.0128 \sqrt{98.5 \times 298} \\ &= 0.0128 \sqrt{29.300} = 2.19 \text{ D.} \end{aligned}$$

10. Beilstein, 12, 11, 339.
11. L. Denivelle, Bull. soc. chim. France, [5], 3, 2143 (1936).
12. L. F. Audrieth and M. von Brauchitsch, J. Org. Chem., 21, 426 (1956).
13. M. Battagay and L. Denivelle: Bull. soc. chim. France, [4], 53, 1242 (1933).
14. M. Battagay and J. Meybeck: Compt. rend., 194, 186 (1932).
15. J. Meybeck: Ann. chim., [10], 17, 129 (1932).
16. M. Battagay, L. Denivelle and J. Meybeck: Compt. rend., 193, 1195 (1931).
17. A. Siwoloboff; Ber., 19, 795 (1886).
18. M. L. Judd: Doctoral Thesis, University of Illinois, Urbana, Illinois (1958).
19. F. H. Winslow and W. J. Matyerik: Polymer Science, 22, 315 (1956).
20. L. F. Audrieth, M. Sveda, H. H. Sisler, and J. Butler: Chem. Revs., 26, 49 (1940).
21. W. Traube: Ber., 24, 360 (1891).
22. R. Wegler and K. Bodenbenuer: Ann. Chem., 624, 25 (1959).
23. A. E. Hill: J. Am. Chem. Soc., 53, 2958 (1931).
24. L. Denivelle: Bull. Soc. Chim. France, [5], 3, 2143 (1936).
25. R. Beherend: Ann., 222, 116 (1884).
26. F. Feher and H. J. Berthold: Z. anorg. u. allgem. Chem., 273, 144 (1953).
27. R. J. A. Otto: WADC Technical Report 58-51, ASTIA Document No. 151177, p. 118, April 1958.
28. E. L. Wittbecker and P. W. Morgan, J. Polymer Science, 50, 289(1959).
29. S. A. Sundet, W. A. Murphey, and S. B. Speck, J. Polymer Science, 50, 389 (1959).
30. F. C. Wood and A. E. Battye, J. Soc. Chem. Ind., 52, 3467 (1933).
31. A. Max. Porquin: Angew. Chem., A 60, 316 (1948).
32. G. Hecht and H. Henecka: Angew. Chem., 61, 365 (1949).
33. M. Goehring, J. Heinke, H. Malz, and G. Roos: Z. anorg. u. allgem. chem., 273, 200 (1953).
34. A. V. Kirsanov and Yu. M. Zolotov: Zhur. Obshehei Khim., 20, 1650 (1950).

35. A. V. Kirsanov: J. Gen. Chem. U.S.S.R., 22, 101 (1952).
36. A. V. Kirsanov: Ibid., 22, 1389 (1952).
37. A. V. Kirsanov and Z. D. Kekrasova: Zhur. Obshchei. Khim., 27, 1253 (1957).
38. G. M. Kosolapoff: J. Am. Chem. Soc., 64, 2982 (1942).
39. K. A. Petrov, N. K. Bliznyuk, and V. P. Korotkova, J. Gen. Chem. U.S.S.R., 30, 2967 (1960).
40. F. Ephraim and M. Gurewitsch: Ber., 43, 138 (1910).
41. A. V. Kirsanov: J. Gen. Chem. U.S.S.R., 22, 101 (1952).
42. W. Traube, Ber., 25, 2472 (1892).
43. A. Hantasch and A. Holl: Ber., 34, 3430 (1901).
44. R. Appel and M. Goehring: Z. anorg. chem., 271, 171 (1953).
45. H. Malz: Dissertation, Heidelberg (1954).
46. A. V. Kirsanov: Zhur. Obshchei. Khim., 22, 88 (1952).
47. A. V. Kirsanov: Ibid., 22, 81 (1952).
48. M. Goehring, J. Heinke, H. Malz and G. Roos: Z. anorg. chem., 273, 200 (1953).
49. M. Goehring and H. Malz: Z. Naturforsch, 9b, 567 (1954).
50. A. J. Banister and A. C. Hazell: Proc. Chem. Soc., 1962, 282.
51. F. Seel and G. Simon: Angew. Chem., 72, 709 (1960).
52. J. W. Smith: Electric Dipole Moments, Butterworths (1955).
53. P. J. Wheatley: "The Determination of molecular structure", Chapter XI, Oxford Press, 1959.
54. B. A. Brice and M. Halwer: J. Opt. Soc. Am., 41, 1033 (1951).